IRON AND STEEL
INSTITUTE PAPERS

PLANT DESIGN · MANUFACTURE · RESEARCH · DEVELOPMENT

Effect of Cooling Rate and Composition on the Embrittlement of Weld Metal

By E. C. Rollason, Ph.D., M.Sc., F.I.M., and R. R. Roberts, M.A., L.I.M.

SYNOPSIS

Tensile specimens of extremely rapidly cooled (e.g., 1400° C./min.) mild steel weld metal have low ductility associated with woody fractures. In welds with high hydrogen content, micro-fissures similar to hair-line cracks are also found, and these prevent the complete recovery of ductility by tempering at 650° C. The extent of fissuring has been shown to be related to the hydrogen and nitrogen contents of the weld.

It is suggested that fissuring is caused by the embrittling effect of hydrogen on regions of the weld already reduced in ductility by the presence of carbon- and nitrogen-rich intermediate transformation products of austenite.

A study has been made of the effects, on fissuring and on nitrogen solubility, of alloy additions to weld metal. Rates of cooling sufficient to cause embrittlement are likely to arise in relatively few welding operations, but when welding thick plates under conditions liable to intensify the cooling of a weld, it is recommended that a preheat of 100° C. be used.

THIS work deals with the properties of mild steel weld metal produced by the metallic-arc process using coated electrodes. Such arc welds are characterized by high yield strengths together with good ductility, although the carbon and manganese contents usually do not exceed 0·13% and 0·6% respectively. This is caused partly by the constitution and partly by the high rate of cooling of the metal from its freezing point. The deposition of a small bead of metal on a massive plate can produce quenching rates from the liquid state far higher than those usually met with in common metallurgical treatments. In normal practice the welding technique is such that the rate of cooling of the weld is not so excessive as to affect adversely the mechanical properties of the weld. Thus, the size of the electrode, multi-run sequence, and preheating temperature are related to the plate thickness being welded.

On the other hand, it is known that exceptionally rapid cooling can reduce the ductility of arc welds, although the tensile strength is not appreciably affected. Some specimens wnich had been quenched very drastically were found to contain fissures. The use of the quenching treatment arose out of other work on the welding of high-tensile steels in which water cooling was employed. In the Rollason heat sink test for weldability[1] the plate is partially immersed in water, which tends to produce an exceptionally steep temperature gradient when plates of thickness less than ½ in. are used. In the production of weld samples for the estimation of hydrogen, it was thought desirable to minimize loss of gas by depositing the weld on a thin plate, the bottom of which was cooled with a jet of water.

Using these methods of obtaining high quenching rates, a study was made of some of the factors affecting the ductility of welds. Before the work was completed, Flanigan[2] and Bland[3] reported that mild steel arc-weld deposits which had been quenched after the completion of welding showed considerably less ductility than those which were allowed to cool normally in air, and that this was caused by the presence of small fissures.

FORM OF FISSURE

Figures 6*a* and *b* show sections through two multi-run welds ; in (*a*) the sample was welded normally, and in (*b*) continuous water-cooling was used during welding. The macro-sections were etched for 3 min. in boiling HCl, to reveal and exaggerate the fissures. The fractures of all-weld metal tensile specimens

Manuscript received 17th December, 1949.

Dr. Rollason is Director of Research, Murex Welding Processes, Ltd., Waltham Cross. Mr. Roberts is a metallurgist at British Thomson-Houston, Ltd., Rugby, and was formerly an assistant in the Research Department, Murex Welding Processes, Ltd.

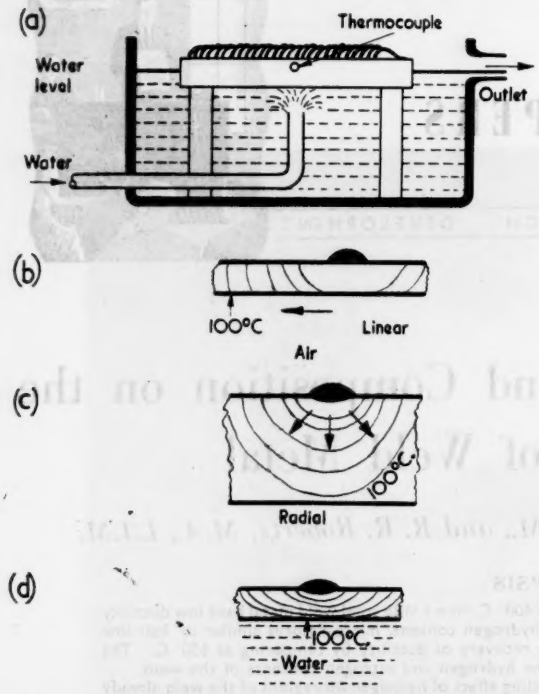


Fig. 1—Formation of weld beads. (*a*) Method (diagrammatic) of rapidly cooling the bead during deposition; (*b–d*) various forms of heat flow

are shown in Figs. 9*a* and *b*, the latter having typical faceted areas.

Micro-examination of polished specimens revealed no cracks, but after etching in 2% nital numerous fine fissures were revealed in the quenched specimens, as typified in Fig. 7 for an unrefined single bead, and Fig. 8 for a bead subsequently heated by other runs. The cracks are mainly transcrystalline, and the absence of heat tinting of the fractured surface indicates that the cracks occur at a relatively low temperature and should not be confused with the so-called 'hot' cracks, which are intercrystalline.

EXPERIMENTS EMPLOYING DIFFERENT RATES OF COOLING

Numerous coated electrodes were used in this work, and the type of flux covering is defined by the Institute

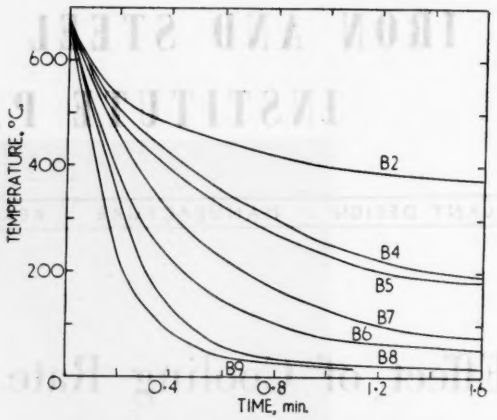


Fig. 2—Cooling rates of weld beads

of Welding—British Electrical and Allied Manufacturing Association's classification of mild steel electrodes.*

The approximate cooling rates of weld beads, 3 in. long, deposited on different-sized plates, some of which were water-cooled, have been obtained from a thermocouple placed approximately $\frac{1}{16}$ in. from the weld junction (*see* Fig. 1*a*). The electrode used had Code No. E217.

The first series of tests (B2–B6) was on plates of varying size, details of which are given in Table I. The cooling curves (Fig. 2) demonstrate the increase of cooling rate with the mass and thickness of the base plate. The thickness of plate for a given mass is the more important factor, since the change from linear to radial heat flow intensifies the rate of cooling of the weld bead, *i.e.*, the temperature gradient is steeper (Figs. 1*b* and *c*).

The second series (B7, B8, B9) was on small plates of various thicknesses. For these, however, cooling was accelerated by immersing the plates to a depth of $\frac{1}{8}$ in. in running water, with a jet of water playing on the underside of the plate; the arrangement

* 1st Digit of Code defines the flux coating as follows:
1 = Cellulosic (thin slag)
2 = Rutile (viscous slag)
3 = Rutile (fluid slag)
4 = Oxide/silicate (inflated slag)
5 = Oxide/silicate (heavy solid slag; rich in iron oxide)
6 = Lime/fluoride (glassy slag)

Table I

EFFECT OF COOLING RATE ON FISSURE FORMATION

Test No.	Size of Plate, in.	Weight of Plate, kg.	Cooling	Fissures/Section	Extent of Heat-Affected Zone, in.	Temperature after $\frac{1}{2}$ min., °C.
B2	$3 \times 2 \times \frac{1}{2}$	0·4	Air	...	0·17	465
B4	$15 \times 18 \times \frac{1}{2}$	18·0	,,	...	0·15	385
B5	$24 \times 18 \times \frac{1}{2}$	28·0	,,	...	0·16	355
B6	$8 \times 9 \times 3$	28·0	,,	20	0·08	180
B7	$3 \times 1 \times 1$	0·4	Water	...	0·12	260
B8	$3 \times 2 \times \frac{1}{2}$	0·4	,,	80	0·07	90
B9	$4 \times 2 \times \frac{3}{8}$	0·4	,,	80	0·07	55

Table II

EFFECT OF ELECTRODE GAUGE ON FISSURING

Electrode Gauge	Plate Size 12 in. × 18 in. × 1 in. (28 kg.)		Plate Size 12 in. × 9 in. × 2 in. (28 kg.)	
	No. of Fissures	Max. Width Heat-Affected Zone, in.	No. of Fissures	Max. Width Heat-Affected Zone, in.
12	10	0·08	10	0·07
10	5	0·10	10	0·09
8	...	0·11	5	0·10
6	...	0·13	...	0·12
4	...	0·14	...	0·13

is shown in Fig. 1*a*. Figure 2 gives the cooling curves for this series. Unlike the previous series, the thinner plates provide the highest rate of cooling, since the bottom of the plate tends to be maintained at the temperature of the water and a very steep temperature gradient is formed (Fig. 1*d*).

All deposits were sectioned and etched in 50% HCl, to determine whether they were fissured.

The results show that fissures will form at the cooling rate shown in Curve B6, but not at that shown in Curve B7. That is, if the weld reaches 100° C. in less than one minute, it will be fissured.

To obtain conditions more closely resembling those existing in practice, experiments were conducted on large plates, in air, using different gauge electrodes of the E217 type to deposit beads 3 in. long. The results are given in Table II.

It will be seen that on 1-in. plate of the size used, deposits from very small gauge electrodes (Nos. 12 and 10 gauge) only will be fissured, whilst on 2-in. plate the No. 8 gauge deposit is also fissured. Such small gauge electrodes would not normally be used on these plates.

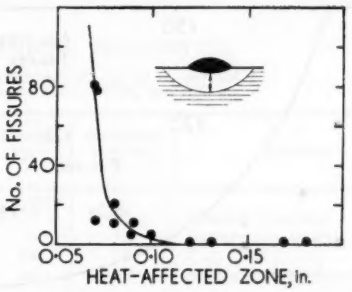


Fig. 3—Relation between the number of fissures and the width of the heat-affected zone

There is a direct correlation between the rate of cooling and the extent of the heat-affected zone. The figures for the extent of this zone indicate that fissuring is probable where the width of the zone is less than 0·11 in.; this may be of considerable importance to an inspector, since it is possible to estimate the approximate width of the heat-affected zone from the surface of a joint. Figure 3, which includes results from Tables I and II, shows this effect clearly.

INFLUENCE OF TYPE OF ELECTRODE

To ascertain some of the fundamental reasons for the formation of fissures, a number of experiments have been conducted using various electrodes, many of which were experimental types. The method adopted was to deposit a 3-in. bead with a No. 6 gauge electrode on $\frac{3}{8}$-in. plate partially immersed in running water, with a water jet on the underside of the plate. In addition, several welds were made under water, to reduce the nitrogen content and increase

Table III

EFFECT ON FISSURING OF DIFFERENT TYPES OF ELECTRODE WELDED IN AIR AND UNDER WATER

Test No.	Welding Conditions	Electrode						Approx. No. of Fissures/Section
		Type	Deposit Analysis					
			C, %	Mn, %	N_2, %	Mo, %	H_2, c.c./100 g.	
C 1	In air	E217	0·035	0·55	0·028		21·1	80
C 2	,,	,,	0·065	0·40	0·080		10·8	30
C 3	,,	,,	0·080	0·57	0·030		18·7	10
C 4	,,	,,	0·075	0·55	0·050		18·0	25
C 5	,,	,,	0·035	0·56	0·052		10·4	20
C 6	,,	E116	0·085	0·58	0·023		41·1	100
C 7	,,	E437	0·100	0·33	0·028		16·6	60
C 8	,,	E537	0·010	0·03	0·033		4·4	...
C 9	,,	E645	0·068	0·86	0·020	0·6	2·2	...
C10	,,	,,	0·062	0·96	0·050	0·6	2·6	...
C11	,,	,,	0·065	0·81	0·024	0·6	9·0	...
C12	,,	,,	0·085	0·90	0·019		2·3	...
C13	,,	,,	0·070	0·84	0·052		2·4	...
C14	,,	,,	0·070	0·78	0·018		7·8	...
D 1	Under water	E217	0·045	0·20	0·010		24·6	15
D 2	,,	E537	0·015	0·03	0·011		22·3	15
D 3	,,	E645	0·040	0·32	0·009	0·6	20·1	...

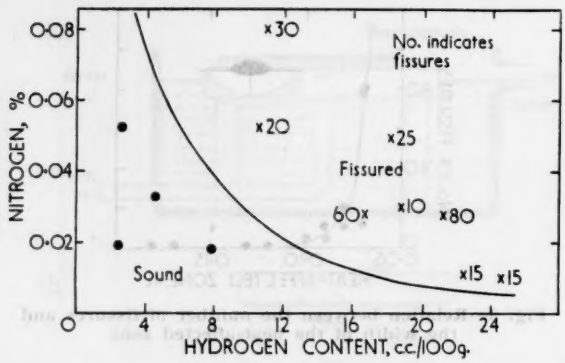


Fig. 4—Relation between nitrogen and hydrogen contents and the number of fissures

the hydrogen content. The number of fissures was estimated from sections of the bead etched in 50% HCl; results are given in Table III.

These results are particularly interesting in relation to the chemical analyses of the various deposits. The analyses were made on millings taken from pads, hydrogen determinations being made on sections cut from the same pads. Although the values are likely to differ somewhat from the hydrogen content of a single bead, the order will be roughly the same.

It appears that hydrogen and nitrogen affect the tendency to cracking; Fig. 4 has therefore been plotted to show the number of fissures for both nitrogen and hydrogen. If the content of one of these elements is low, the content of the other can be high without promoting fissuring, but high hydrogen is more damaging than high nitrogen.

Table IV

EFFECT OF ALLOYS ON FISSURE FORMATION

(Welds with normal high hydrogen contents; *i.e.*, H_2 = 15–20 c.c./100 g.; N_2 = 0·03%, approx.)

Test No.	Alloy Content, %	Fissures/Section	Hardness, V.P.N.
E 1	0·15 Mo	30	258
E 2	0·32 Mo	15	267
E 3	0·82 Mo	...	276
E 4	1·65 Mo	10	279
E 5	2·50 Mo	80	280
E 6	3·50 Mo	100	286
E 7	0·24 Cr	30	247
E 8	0·36 Cr	25	250
E 9	0·81 Cr	40	297
E10	0·35 V	25	265
E11	0·43 V	50	271
E12	0·48 V	70	294
E13	0·52 Ni	80	253
E14	1·06 Ni	80	275
E15	1·37 Ni	80	282
E16	0·06 Mn	...	210
E17	0·15 Mn	...	215
E18	0·24 Mn	40	225
C 1	0·55 Mn	80	234
E19	0·86 Mn	80	250
E20	1·25 Mn	80	303
E21	1·85 Mn	80	320

THE EFFECT OF ALLOYS ON FISSURE FORMATION

The results for the deposits containing molybdenum suggested that molybdenum was giving some protection against fissure formation. Tests were carried out, therefore, on E217-type deposits containing varying amounts of molybdenum, so as to determine its protective effect in the presence of normal hydrogen and nitrogen contents. Tests were also carried out on deposits containing chromium, vanadium, nickel, and manganese. The results are given in Table IV and are shown graphically in Fig. 5. In other respects the analyses were similar to those in test C1.

The effects of alloying elements on fissuring are summarized as follows:

Molybdenum—Addition of molybdenum to the E217 deposit, containing 0·55% Mn, results in a reduction in the number of fissures, sound deposits being obtained with approximately 0·80% molybdenum. Further addition results in fissured deposits, the number of fissures increasing with increase of molybdenum content.

Chromium and Vanadium—The result of small additions of either of these elements is a reduction in the number of fissures, a minimum of 25 being reached at about 0·35%. Further addition increases the number of fissures.

Nickel—In the nickel range between 0·52% and 1·37%, the number of fissures remained unchanged at the fairly high level of 80.

Manganese—Deposits very low in manganese are not fissured. However, when the manganese content is raised above 0·15%, fissures increase to a maximum at about 0·55%. Increasing the manganese content to 1·85% has no additional effect on the number of fissures.

EFFECT OF RAPID COOLING ON MECHANICAL PROPERTIES

All-weld tensiles were made to BS. 639 (revised draft), using 5-minute intervals between runs, and were compared with tensile specimens made under conditions of rapid cooling (*i.e.*, with plates partially immersed in water). Various electrode types were used and some specimens were heat-treated after welding. Results are given in Table V.

These results show that all five types of weld have considerably reduced ductility when rapidly cooled, although only two types (E217 and E437) had shown fissuring in the single-bead test. Heat-treatment at 650° C. increased the ductility, but not up to the

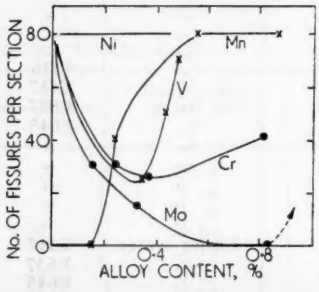


Fig. 5—Effect of alloy content on the number of fissures

Table V

EFFECT OF RAPID COOLING ON MECHANICAL PROPERTIES

Welds deposited from E217 and E437 electrodes contain approximately 20 c.c. of H_2 per 100 g.
Welds deposited from E645 electrodes contain approximately 3 c.c. of H_2 per 100 g.

Electrode	Cooling	Heat-Treatment	Yield Point, tons/sq. in.	U.T.S., tons/sq. in.	Elongation, %	Reduction of Area, %	Fracture
E217	Normal	As welded	27·8	33·5	27	45	Haloes present
	Rapid	,, ,,	29·9	31·9	6	12	Extensive brittle areas
	Normal	16 hr. at 650° C.	25·5	28·5	40	70	Cup and cone
	Rapid	,, ,, ,,	23·5	28·2	29	40	Many brittle areas
E217-Mo	Normal	As welded	35·9	41·6	18	33	Haloes present
	Rapid	,, ,,	35·7	35·7	2	4	Extensive brittle areas
E437	Normal	As welded	26·0	28·5	31	45	Haloes present
	Rapid	,, ,,	26·0	28·5	11	17	Brittle areas
	Normal	1 hr. at 650° C.	24·0	28·7	38	65	Cup and cone
	Rapid	,, ,,	23·0	28·5	25	37	Partially brittle
E645	Normal	As welded	30·2	33·7	33	65	Cup and cone
	Rapid	,, ,,	32·6	34·0	10	16	Extensive brittle areas
E645-Mo	Normal	As welded	35·1	38·9	26	62	Cup and cone
	Rapid	,, ,,	39·1	40·6	9	17	Extensive brittle areas
	Normal	16 hr. at 650° C.	31·1	34·3	32	73	Cup and cone
	Rapid	,, ,, ,,	34·3	37·4	21	36	Partially brittle

value obtained on a heat-treated specimen welded in the normal manner. It seems possible, therefore, that the other three types of weld are also fissured in multi-run deposits, although they are sound in single runs.

To confirm the absence of fissures in single runs from E645 and E217 Mo-containing electrodes, single beads were deposited on ½-in. mild steel and were then tested by bending over a 1½-in. former. Some specimens in the as-welded condition, and others after heat-treatment for 1 hr. at 650° C., were bent until cracked. Results are shown in Table VI.

Tnese results showed that rapid cooling produces a decrease in ductility in all four types of weld, but that all except the Mo-free E217 type show complete recovery on tempering. It is thus confirmed that the low ductility in the other types is not caused by fissuring.

It was thought that low ductility in heat-treated multi-run welds which had shown freedom from fissuring in single runs, may possibly have been caused by segregation of some element, such as sulphur, which diffused so slowly below 1100° C. that heat-treatments in the normal temperature ranges would have little effect. It was therefore decided to carry out high-temperature heat-treatments (up to 1400° C.) on E645-Mo deposits, to see whether redistribution of some constituent occurred. Quenching from 1200° C. was used to simulate the rapid cooling of a weld. Heat-treatment was carried out on normal and rapidly cooled specimens. Results are given in Table VII.

The results showed that no further recovery is brought about by high-temperature heat-treatment, and it seemed probable that the lack of ductility in these rapidly cooled multi-run deposits was caused by fissuring. If this were so, forging at high temperatures should bring about some recovery of ductility, owing to the welding of such fissures. Therefore, specimens of E645-Mo, both normally cooled and rapidly cooled, were forged at 1200–900° C., prior to tensile testing. After forging, specimens were water-quenched from about 1000° C. and tempered for 1 hr. at 650° C. Results are given in Table VIII.

It will be seen that forging to a 40% reduction of area has brought about a considerable, though not a complete, recovery in ductility. At the same time the shear type of fracture has been replaced by a much more ductile fracture with only minute brittle zones, as illustrated in Fig. 9*e*.

Table VI

EFFECT OF RAPID COOLING ON DUCTILITY OF SINGLE-BEAD BEND TESTS

Electrode	Cooling	Heat-Treatment	Angle of Bend
E217	Normal	As welded	180°
,,	Rapid	As welded	18°
,,	Rapid	1 hr. at 650° C.	70°
E217-Mo	Normal	As welded	180°
,,	Rapid	As welded	11°
,,	Rapid	1 hr. at 650° C.	180°
E645	Normal	As welded	180°
,,	Rapid	As welded	44°
,,	Rapid	1 hr. at 650° C.	180°
E645-Mo	Normal	As welded	180°
,,	Rapid	As welded	40°
,,	Rapid	1 hr. at 650° C.	180°

Table VII

EFFECT OF HIGH-TEMPERATURE HEAT-TREATMENT ON E645 DEPOSITS

Welds deposited from E645 electrodes contain approximately 3 c.c. of H_2 per 100 g.

Electrode	Cooling	Heat-Treatment*	Yield Point, tons/sq. in.	U.T.S., tons/sq. in.	Elongation, %	Reduction of Area, %	Fracture
E645-Mo	Normal	½ hr. at 1200° C.	35·2	41·4	26	69	Cup and cone
,,	Rapid	,, ,, ,,	35·0	38·4	11	18	Partially brittle
E645-Mo	Normal	½ hr. at 1300° C.	41·4	47·8	13	62	Cup and cone
,,	Rapid	,, ,, ,,	44·1	44·6	5	13	Partially brittle
E645-Mo	Normal	½ hr. at 1400° C.	45·3	48·1	21	61	Cup and cone
,,	Rapid	,, ,, ,,	...	44·6	6	14	Partially brittle

* All specimens were water-quenched from 1200° C. and tempered for ½ hr. at 650° C.

The brittle areas in heat-treated specimens made from E645 electrodes appeared to be confined to certain runs (*see* Fig. 9*d*). This suggested that fissuring had taken place only in such runs, and subsequent micro-examination confirmed the presence of a few fissures. It was concluded that composition conditions for fissuring are not fulfilled in single runs from E645 and E217-Mo electrodes, but that in multi-runs such conditions will eventually be fulfilled and fissuring will occur, provided that the rate of cooling is sufficiently high. The three elements concerned in the fissuring in these cases are H_2, N_2, and Mo. To determine which of these elements is responsible for fissuring under multi-run conditions, all-weld metal tensiles were made from E645 electrodes in which each run was quenched by welding with the plates partially immersed in water and then heat-treated at 650° C. for 1 hr. to remove hydrogen, before the application of the next bead. This heat-treatment will have no effect upon the concentration of nitrogen in the specimen. Results are given in Table IX.

Since both types of weld show normal ductility under these conditions, it is clear that fissuring is entirely eliminated by heat-treating between runs.

Table VIII

EFFECT OF FORGING ON MECHANICAL PROPERTIES OF E645-Mo DEPOSITS

Cooling	Approximate Reduction of Area by Forging, %	Yield Point, tons/sq. in.	U.T.S., tons/sq. in.	Elongation, %	Reduction of Area, %
Normal	30	...	35·2	25	65
Normal	40	30·5	35·8	29	70
Rapid	25	30·6	35·8	18	24
Rapid	40	30·6	35·8	24	56

The only element which will be affected by the heat-treatment is hydrogen, which will be removed. It is suggested, therefore, that when multi-run deposits are made from electrodes which produce unfissured single beads there is a gradual increase of hydrogen content in each succeeding bead until a stage is reached at which the hydrogen content is sufficient to cause fissuring. Once fissures have been formed the hydrogen will be locked in the actual fissures, and the building-up process will have to recommence.

MICROSTRUCTURE

Sections were prepared for micro-examination so as to ascertain the differences between normally cooled and quenched specimens. All normally cooled specimens showed separation of massive nitrides, as in Figs. 10*a* and 11*a*. In the rapidly cooled specimens much less nitride had separated out, as in Figs. 10*b* and 11*b*. The differences between reheated beads (Figs. 11*a* and *b*) and the unrefined structures (Figs. 10*a* and *b*) are also shown.

The addition of molybdenum, however, appeared to promote the formation of nitrides even in quenched specimens. This led to the study of the effect of various elements on the formation of nitrides. A number of deposits were made of the E217 electrode, to which various elements were added. Each electrode was deposited using (*a*) a short arc to give nitrogen of the order of 0·02–0·03%, and (*b*) a long arc to give nitrogen of the order of 0·05–0·06%. The analyses of these deposits are given in Table X.

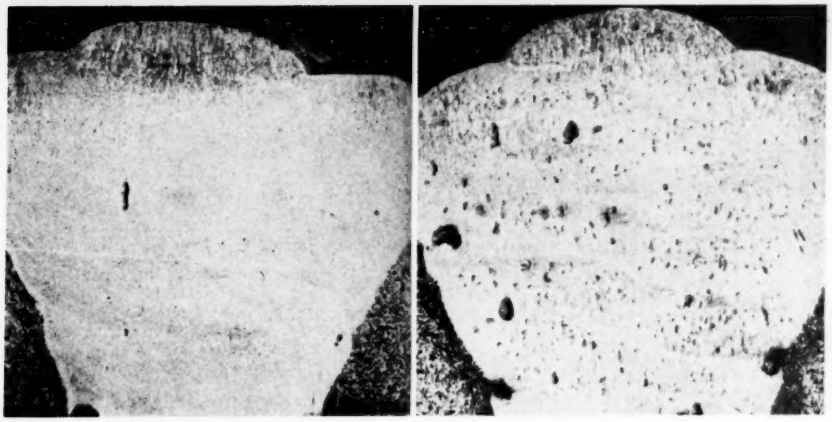
The deposits were made in the form of pads, which were heat-treated at 900° C. for 1½ hr. and then allowed to cool very slowly in the furnace, the time for cooling from 900° C. being approximately 20 hr. After this annealing treatment, sections were prepared for micro-examination. Subsequently, samples were reheated at temperatures in the range 200–600° C.

Table IX

EFFECT ON MECHANICAL PROPERTIES OF HEAT-TREATMENT OF EACH RUN OF RAPIDLY COOLED DEPOSITS

Electrode	Yield Point, tons/sq. in.	U.T.S., tons/sq. in.	Elongation, %	Reduction of Area, %	Fracture
E645	28·0	31·5	39	72	Cup and cone
E645-Mo	37·9	40·3	29	63	Cup and cone

(a)



(b)

Fig. 6—Macrographs of butt welds cooled at different rates (*a*) Normal cooling, (*b*) Rapid cooling Etched in boiling HCl × 2

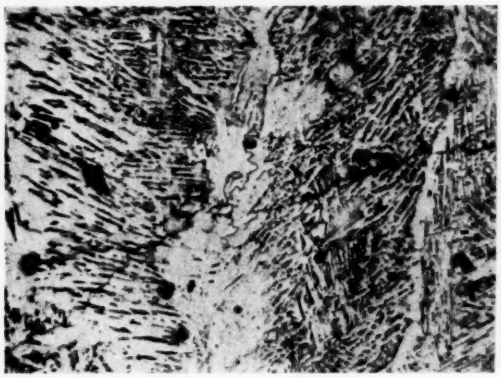


Fig. 7—Fissure in single bead of unrefined weld metal. Etched 2% nital × 500

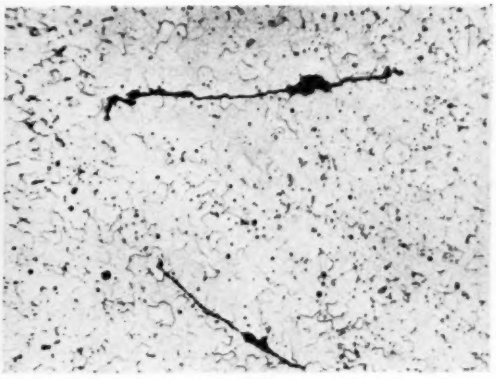


Fig. 8—Fissures in refined area of multi-run weld. Etched 2% nital × 250

[*Rollason and Roberts*
[*To face p.* 110

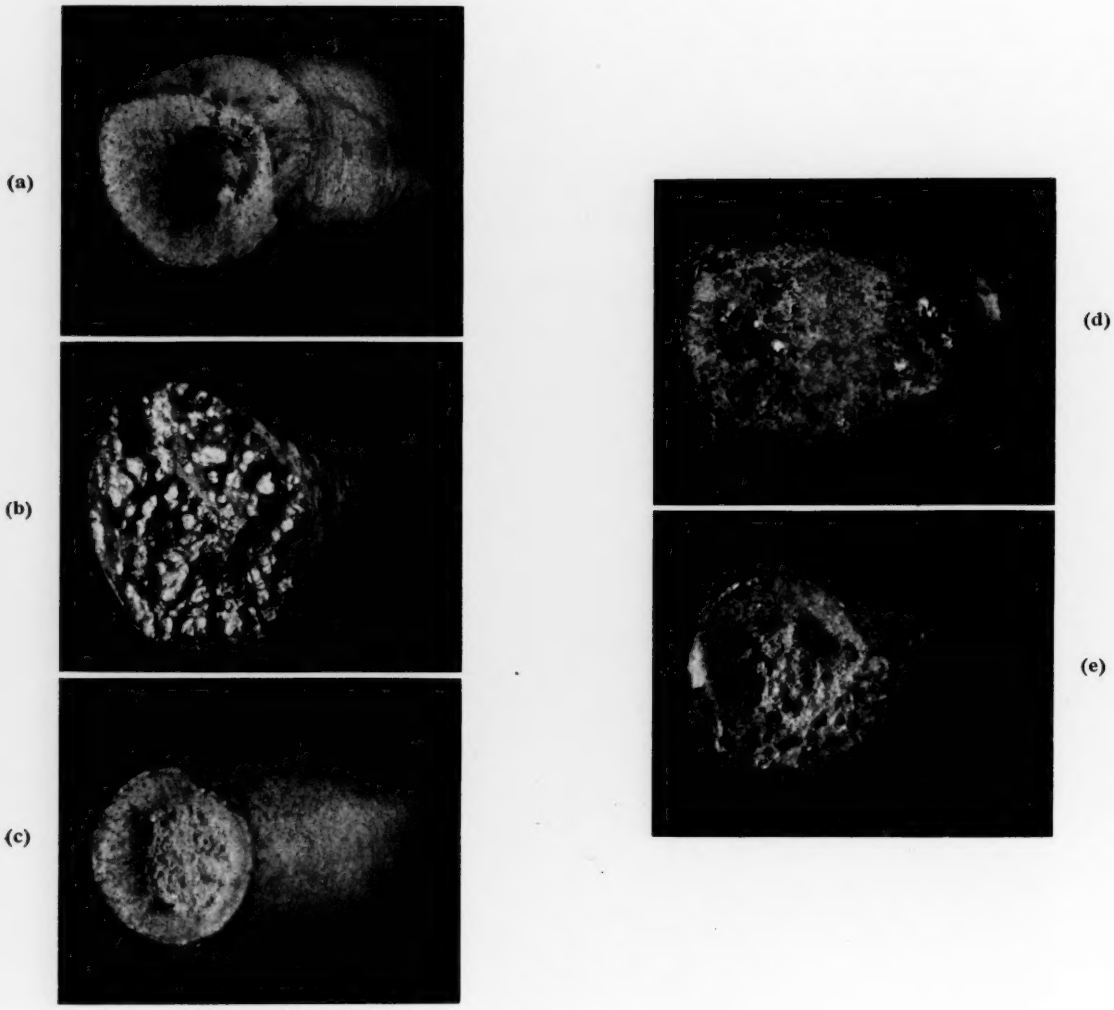
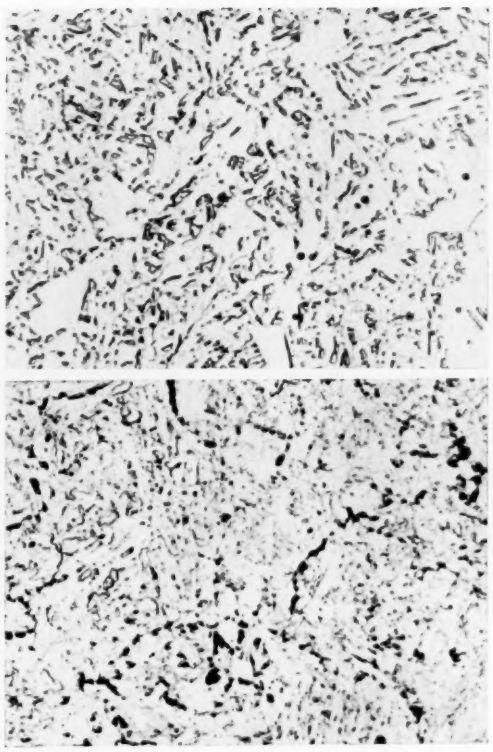


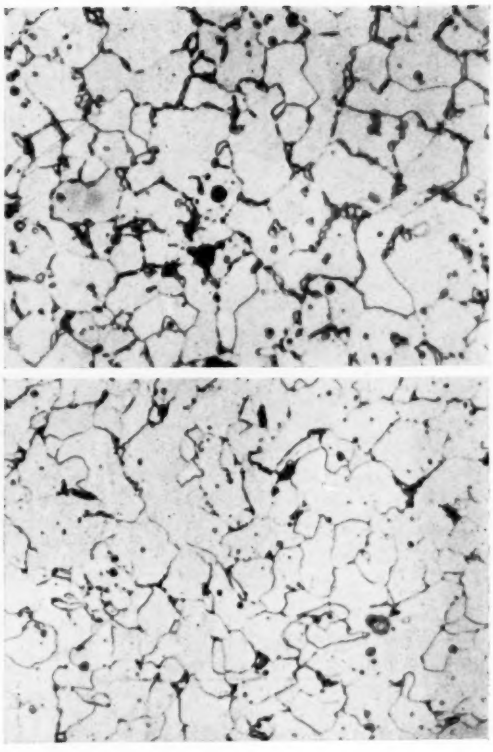
Fig. 9—Fractures of all-weld specimens. E217 electrodes have high rutile content ; E645 electrodes have lime-fluospar base giving low hydrogen weld metal × 4

(*a*) **E217 deposit, normally cooled**
(*b*) **E217 deposit, rapidly cooled as welded**
(*c*) **E645 deposit, normally cooled**
(*d*) **E645 deposit, rapidly cooled and heat-treated**
(*e*) **E645 deposit, rapidly cooled and hot forged**

(a)

(b)





(a)

(b)

Fig. 10—Unrefined areas in E645-Mo deposits. Etched 2% nital × 750
(*a*) Normally cooled
(*b*) Cooled on water bath. Note dark etching constituents in form of network

Fig. 11—Refined areas in E437 deposits. Etched 2% nital × 750
(*a*) Normally cooled
(*b*) Cooled rapidly

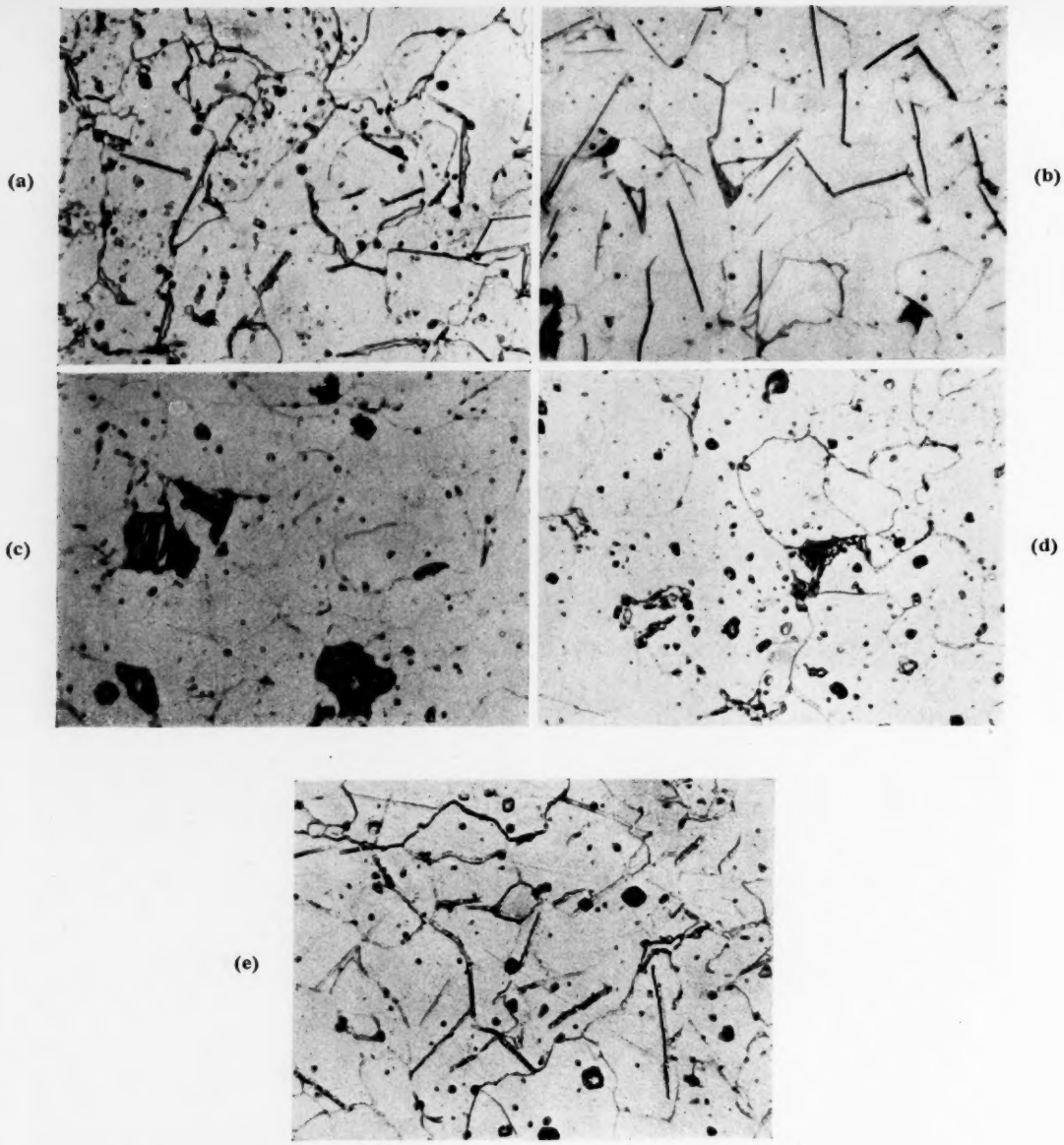


Fig. 12—Microstructures of weld metals annealed at 900° C. and slowly cooled ; using E217 type flux with alloy contents as shown in Table X (*a*) F1, alloy-free (nitrides and carbides in ferrite) ; (*b*) F3, 0·55% manganese; (*c*) F6, 0·80% molybdenum; (*d*) F7, 0·48% chromium; (*e*) F9, 1·06% nickel × 750

Table X
ANALYSIS OF DEPOSITS FOR MICRO-EXAMINATION

No.	C, %	Mn, %	Cr, %	Mo, %	Ni, %	N_2, %
F 1	0·029	0·06	...	...	...	0·031
F 2	0·030	0·03	...	...	...	0·052
F 3	0·026	0·55	...	...	...	0·020
F 4	0·030	0·31	...	...	...	0·056
F 5	0·030	0·06	...	0·80	...	0·021
F 6	0·027	0·06	...	0·80	...	0·035
F 7	0·032	0·03	0·48	...	...	0·028
F 8	0·032	0·04	0·42	...	...	0·052
F 9	0·028	0·03	...	...	1·06	0·025
F10	0·027	0·03	...	...	1·20	0·049

for 1 hr. and were quenched in iced brine, to examine the solubility of the nitrides under practical rather than equilibrium conditions. Figures 12*a–e* give microstructures of five weld metals, one for each alloy group, in the annealed condition. The effect of the added elements on the nitride formation may be summarized as follows :

(*a*) *Manganese*—This element appears to give an increased amount of precipitated nitrogen in the form of needles (Fig. 12*b*). The specimen with higher nitrogen (F4) showed a small amount of braunite (iron–nitrogen eutectoid). On reheating, the needles in specimen F3 dissolved at approximately 300° C., whilst those in F4 required 600° C. No braunite was observed in specimen F2 and again a temperature of 600° C. was required for complete solution of nitrogen needles, but only a few needles were present after reheating to 500° C.

(*b*) *Molybdenum*—In the molybdenum-containing deposits most of the nitrogen occurs in the form of a eutectoid ; an increase in nitrogen merely increases the amount of eutectoid present in the structure (Fig. 12*c*). The small solubility of isolated nitrides indicates a steeper solubility curve for nitrogen in welds containing 0·80% of molybdenum than in molybdenum-free welds.

(*c*) *Chromium*—A small amount of eutectoid constituent is to be seen in the microstructures of both chromium-containing welds. More isolated nitride in the form of needles is present than in molybdenum-bearing steels (Fig. 12*d*). Chromium causes a smaller decrease in solubility of nitrides than does molybdenum.

(*d*) *Nickel*—In the nickel-containing steels, the number of nitrogen needles is smaller than in the alloy-free welds and they dissolve at relatively low temperatures (Fig. 12*e*).

The approximate solubility curves for nitrogen in the five types of weld metal are shown qualitatively in Fig. 13.

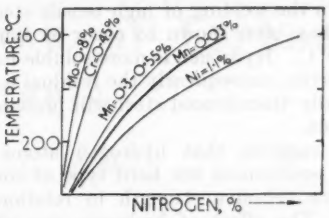


Fig. 13—Effect of alloying elements on approximate solubility of nitrogen

DISCUSSION

Mild steel metallic-arc welds are quite ductile when made with normal welding procedures designed to avoid excessive quenching effects. The rate of cooling of the weld, however, can be greatly intensified by the use of electrodes small in gauge relative to the mass of plate, thick plates, and cold atmospheric conditions. If the rate of cooling is such that the weld deposit reaches 100° C. in less than one minute, very low ductility of the weld results. Such rates of cooling are similar to the highest rates met with in heat-treatment practice (*i.e.*, water-quenching of small sections). It is therefore of the utmost importance in welding practice that attention should be paid to the rate of cooling of the weld bead ; where high cooling rates are expected and heat cannot be concentrated locally by such procedures as block welding, preheating up to 100° C. is essential. These conditions occur infrequently, but will be present increasingly as fabrication by welding is extended to thicker plates. In underwater welding the difficulty cannot be completely overcome, and welds made under water cannot be expected to possess high ductility.

It has been shown that the low ductility of rapidly cooled welds is sometimes associated with minute transcrystalline cracks, but low ductility can be produced without actual fissuring. In such conditions ductility can be recovered by tempering at 650° C. Bland[3] stated that in his tests fissures only occurred in longitudinal sections of welds. In the present work, where the rate of cooling was higher than in Bland's, fissures were observed in both longitudinal and transverse sections.*

It has been demonstrated that fissures form below 600° C. When a deposit is made on mild steel partially immersed in water and the specimen is removed immediately on completion of welding (so that the temperature near the crater end is above 600° C.) and then is allowed to cool in air, no fissures are formed near the crater. However, in this experiment the start of the weld run is quenched below 600° C. before removal, and fissures are evident near this end.

In addition to the rate of cooling, factors affecting fissure formation are carbon, nitrogen, hydrogen, and alloy contents of the weld. Carbon and nitrogen exert most influence in steels by promoting thermal hardening. Rapid quenching of weld metal tends to retain, down to subcritical temperatures, islands or films of austenite rich in carbon and nitrogen. This austenite will transform to intermediate constituents (*see* Fig. 10*b*) in which the lattice is highly stressed, *i.e.*, hardened. Tempering will bring about recovery owing to the breakdown of the intermediate transformation products. Once regions of the weld are reduced in ductility it is well known that hydrogen can intensify embrittlement and cause cracking, especially when associated with macro-contractional stresses. This is demonstrated by the hard zone

* A typical example is the E217 deposit, where the number of fissures observed was approximately 150/sq. cm. in both sections.

cracking in the welding of high tensile steels. Such cracking has been shown to occur at temperatures below 150° C. Hydrogen is more soluble in austenite than in ferrite, consequently the residual austenite in the partially transformed steel will probably be rich in hydrogen.

Petch[4] suggests that hydrogen atoms take up preferred positions in the hard type of constituents, and reduce cohesive strength in relation to yield strength. The effect of hydrogen can also be explained by the diffusion of hydrogen atoms into rifts, where molecules will be formed and a pressure produced sufficient to rupture the steel. In rapidly cooled welds the hydrogen present will act in a similar manner and, provided that parts of the weld are already embrittled, will produce fissuring if present in sufficient concentration. In welds with low hydrogen content, such as those produced by E645 electrodes, the hydrogen content is insufficient to produce fissuring in single beads. In multi-bead deposits, however, each succeeding run will have a higher hydrogen content, owing to the migration of the gas from the ferrite to the austenite existing at an elevated temperature. A concentration will develop sufficient to cause fissuring. After such fissuring the next bead of weld metal is not usually fissured, and it is assumed that part of the hydrogen in the previous layer is fixed in or around the fissures. This process of concentration up to the point of fissuring can be repeated.

When a fissured layer of weld metal is reheated by the next bead, the hydrogen concentrated around the fissure will probably react with inclusions rich in iron oxide, to form water. In addition, carbon may be removed as in the decarburization of steel in moist hydrogen atmospheres. Such reactions explain the light areas around the fissures in Fig. 8, which are relatively free from inclusions and carbides.

Molybdenum, chromium, and vanadium, in small quantities, reduce fissuring by decreasing the nitrogen solubility, and by preventing its hardening effects (by forming massive nitrides just below the eutectoid temperature). The addition of greater quantities of these elements raises the hardness of the weld and increases the tendency to fissure.

CONCLUSIONS

(1) Extremely rapid cooling of mild steel arc welds reduces their ductility without much effect on the yield and ultimate strengths. This decrease in ductility becomes pronounced when a weld bead is cooled down to 100° C. in less than 1 minute. With such a rate of cooling, the width of the heat-affected zone will be approximately 0·1 in.; this may be useful in inspection.

(2) With such drastic cooling, single beads deposited from all electrodes exhibited embrittlement. Minute fissures were present in some beads.

(3) No fissures were present in single quenched unrefined welds having low hydrogen contents and made with E645 and E537 electrodes. Tempering at 650° C. eliminated the embrittlement. After a number of runs, hydrogen may be sufficiently concentrated to cause fissures.

(4) Fissures were present in single quenched beads made from electrodes depositing weld metal with high hydrogen content (> 12 c.c. per 100 g.). The ductility of such beads is not completely recovered by tempering at 650° C.

(5) The presence of molybdenum, chromium, and vanadium, in small quantities, reduces the number of fissures, but large amounts of these elements increase fissuring.

(6) A relationship exists between the amounts of hydrogen and nitrogen; fissuring increases with increase of either element, but particularly with hydrogen.

(7) It is suggested that fissuring is caused by the embrittling effects of hydrogen on regions of the weld already reduced in ductility by the presence of intermediate transformation products of austenite. The volume and properties of such regions are greatly influenced by nitrogen and carbon contents.

(8) This trouble is liable to occur in only a small percentage of welds in practice. Where conditions are such that fissuring is probable, as in thick plates, preheating to 100° C. is recommended, unless the rate of cooling can be reduced by the adoption of special welding procedures designed to give a high concentration of heat.

Acknowledgments

This work has been carried out in the Research Department of Murex Welding Processes, Ltd., Waltham Cross. Thanks are also due to Mr. H. W. Mance, a former member of the Research staff, for assistance during the preliminary experiments.

References

1. "Symposium on Metallurgy of Steel Welding," p. 95. London, 1947: British Welding Research Association.
2. A. E. FLANIGAN: *The Welding Journal*, 1947, vol. 26, Apr., p. 193-s.
3. J. BLAND: *Ibid.*, 1949, vol. 28, May, p. 216-s.
4. N. J. PETCH: "Symposium on Internal Stresses in Metals and Alloys," p. 441. London, 1948: The Institute of Metals.

Nimonic 90

The Mond Nickel Company, Ltd., announce the addition of Nimonic 90 to the published Nimonic series of alloys. Although this superior material has already been installed on many gas turbines, its use has been restricted and details of its properties have not so far been available for publication because of a security ban.

Nimonic 90 results from extensive research in the laboratories of the Company, combined with long production experience in the rolling mills of Henry Wiggin and Company, Ltd. Many service trials have demonstrated its superiority as a material for gas-turbine blades. At 750° C. it is 10% better than Nimonic 80*A* under all conditions. At 815° C., and even at 870° C., it has shown high load-carrying capacity for long periods.

Nimonic 90 is available in bar, sections, forgings, sheet strip, and wire.

The Accurate Determination of Carbon in Low-Carbon Steels

By J. E. Wells, B.Sc., A.R.I.C., A.Met.

SYNOPSIS

An apparatus for the accurate determination of carbon in low-carbon steels is described. The method is based on the use of a liquid-oxygen trap for the isolation of carbon dioxide produced by burning the steel in oxygen. The quantity of carbon dioxide formed is subsequently estimated by measuring the pressure exerted when it is confined to a known volume.

The apparatus gives reproducible results of at least the same order of accuracy as those obtained by other low-pressure methods, and has the merit of simplicity. A combination of one combustion unit with two liquid-oxygen traps enables one carbon determination to be completed every twenty minutes. The method can also be used for the micro-determination of carbon, using sample weights of 0·02 g.

Introduction

THE accurate determination of carbon in steel has been a matter of concern for a number of years. With the development of stainless steels and silicon steels of progressively lower carbon contents, this problem has assumed even greater importance. The first major advance in technique was by Yensen,[1] who developed the low-pressure combustion method. Although this permitted the accurate determination of carbon in steel, the apparatus was complex, and the time for a single determination was long. This type of apparatus has since been modified by Ziegler,[2] Wooten and Guldner,[3] Murray and Ashley,[4] and Stanley and Yensen.[5] Although the time per determination has been much decreased, the combustion of the steel is carried out under reduced pressure, necessitating high-frequency heating of the sample to obtain high temperatures without the danger of collapse of the combustion tube.

The problem has also been attacked by a number of investigators using entirely different principles. Kalina and Joseph[6] used a method based on the absorption of the carbon dioxide, produced by combustion of the steel, in a solution of barium hydroxide. The excess hydroxide was subsequently titrated with a standard acid solution delivered from a capillary pipette. In Nesbitt and Henderson's[7] method the carbon dioxide produced by combustion was absorbed in a solution of caustic soda and, after acidifying, the evolved carbon dioxide was measured under reduced pressure in a specialized gas-analysis apparatus. Ericsson[8] determined the carbon dioxide absorbed in barium hydroxide solution by an electrical conductivity method.

These methods have the disadvantage that complete absorption of carbon dioxide in barium hydroxide solution is difficult to achieve. Special absorption tubes are necessary, and only slow rates of gas flow can be tolerated.

Consideration of these methods suggested that isolation of the carbon dioxide in a liquid-oxygen trap, followed by measurement of the pressure exerted when the gas was transferred to a calibrated volume, was probably the most accurate method of collecting and measuring the carbon dioxide produced by combustion of the steel. On the other hand, the accurate results obtained by investigators using a normal combustion technique[6–8] suggested that the refinement of combustion under reduced pressure, using high-frequency heating, was unnecessary. It was decided therefore to use an ordinary combustion train followed by a trap suspended in liquid oxygen for isolation of the carbon dioxide. The low-pressure measuring equipment used by Yensen has, however, been modified by using a mercury vapour pump and a Töpler pump to transfer the carbon dioxide from the liquid-oxygen trap to the calibrated measuring bulbs.

APPARATUS

A schematic diagram of the combustion apparatus is shown in Fig. 1. Figures 2 and 3 show the vacuum-measuring system and the absorption bulb, respectively.

For convenience the apparatus is considered in sections.

Oxygen Purification System

This system, which is designed to remove hydrocarbons, carbon monoxide, and water vapour from the cylinder oxygen, contains, in addition to the purification train, a pressure gauge and a mercury safety valve. The oxygen first passes through a silica tube packed with platinized asbestos, maintained at approximately 600° C. Any hydrocarbons or carbon monoxide in the gas are thereby converted to carbon dioxide and water, which are removed by passing the gas through soda asbestos and anhydrone absorption tubes. Measurement of the efficiency of this system showed that the amount of oxygen required for one combustion contains, after treatment, the equivalent of 0·00005% of carbon, calculated on the basis of a sample weight of 2 g. of steel. Whilst this blank is almost three times that obtained by the orthodox Yensen apparatus, it is very small and the purification system is very simple.

Combustion Section

The combustion tube is of an orthodox pattern, 20 in. long × ¾ in. internal dia. It contains a side

Manuscript received 21st November, 1949.

Mr. Wells is at The Steel Company of Wales (Lysaght Works), Ltd., Newport, Mon.

inlet tube and is made of ΔH material. The tube is heated over a length of 9 in. by a furnace capable of reaching temperatures up to 1200° C. A glass-wool plug in the exit end of the tube filters out any iron oxide carried out by the gas stream. The combustion boats are 3½ in. long × ½ in. wide, of aluminous refractory material, and are stored in an electric muffle furnace at about 1000° C., being transferred to a desiccator just before use.

An assay-quality lead-sheet flux assists combustion ; it is wire-brushed to remove the surface film and is cut into ¾ × ⅛-in. strips, each strip weighing approximately 0·75 g. The strips are washed in ether, dried in a warm oven, and stored in a covered glass beaker.

After combustion the oxygen is freed from sulphur gases and water vapour by passage through manganese dioxide* and then through an absorption bulb containing anhydrone. The gas issuing from this train is pure oxygen containing the carbon dioxide formed during combustion of the steel, and is passed through the liquid-oxygen trap to isolate the carbon dioxide. The rate of gas flow is controlled by a tap placed just in front of the liquid-oxygen trap.

Isolation Section

This consists of a specially designed absorption tube suspended in a vacuum flask of 1-pint capacity, containing liquid oxygen. The exit end of the absorption tube is connected to a flowmeter *via* a tower containing soda asbestos and anhydrone. This flowmeter registers the rate of gas flow and prevents back diffusion of carbon dioxide and water vapour from the air into the absorption tube.

Design of the Absorption Tube

The first design used is shown in Fig. 4. When using this tube most of the carbon dioxide was frozen out in the inner portion of the central tube, and very consistent results could be obtained on samples containing less than 0·05% of carbon. With steels of higher carbon contents, however, the results were somewhat erratic, and some of the solid carbon dioxide fell to the bottom, instead of remaining in the inner tube. During subsequent evacuation some of this solid was swept out by the gas stream. Attempts to overcome this difficulty by inserting a glass-wool plug in the absorption tube were frustrated by the long time required for evacuation. Absorption tubes were then built to the specifications shown in Fig. 3. These tubes were quite successful, any carbon dioxide falling from the walls of the inner tube dropping into the bottom internal bulb, where it remained undisturbed during subsequent operations. This type of bulb has therefore been used to obtain the results reported in this paper.

* U.S. Steel Corporation, "Sampling and Analysis of Carbon and Alloy Steels," p. 48. New York, 1938 : Reinhold Publishing Corporation.

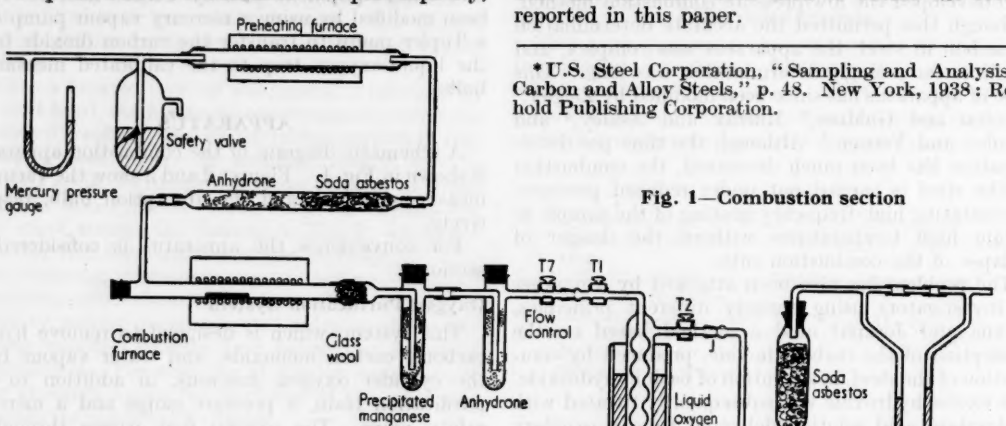


Fig. 1—Combustion section

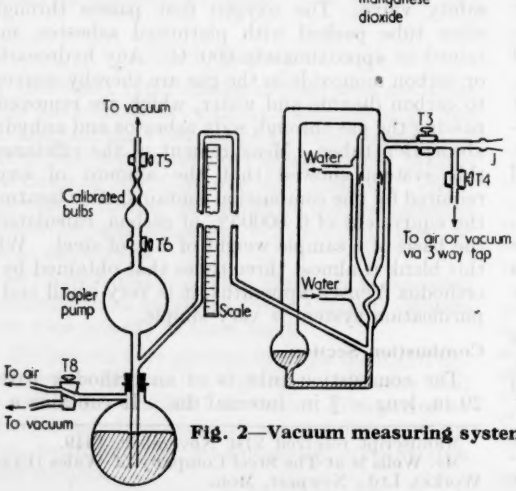


Fig. 2—Vacuum measuring system

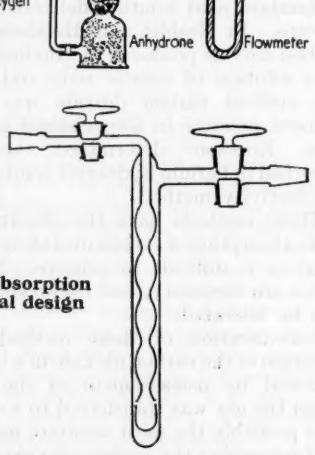


Fig. 3—Absorption bulb, final design

Efficiency of the Liquid-Oxygen Trap

After the removal of the last trace of oxygen from the absorption tube, continued evacuation with the mercury vapour pump does not remove any carbon dioxide from the absorption tube as long as it is maintained at the temperature of liquid oxygen. There is therefore no danger of loss of carbon dioxide at this stage.

Vacuum Measuring System

This consists essentially of a combined Töpler pump and McLeod gauge, in conjunction with a two-stage mercury vapour pump. The absorption bulb is connected to the ground-glass joint *J* (Fig. 2) when the amount of carbon dioxide isolated is to be determined. Provision is made for roughly evacuating the absorption bulb *via* tap *T*4, which leads to the rotary oil pump. The calibrated bulbs have volumes of 0·858, 2·43, and 7·56 ml., covering up to 0·008, 0·024, and 0·1% of carbon, respectively. A pressure-reading of 1 mm. is equivalent to approximately 0·00003, 0·00008, and 0·0002% of carbon, calculated on the basis of a 2-g. sample.

Preparation of Samples

Samples may be obtained by any of the well-known methods, but all samples must be washed in ether; the necessity for this is shown by the following results :

Sample	Carbon, %. Before Washing	Carbon, %. After Washing	Difference
1	0·0190	0·0185	0·0005
2	0·0436	0·0405	0·0031
3	0·0290	0·0269	0·0021
4	0·1000	0·0955	0·0045

PROCEDURE

It is assumed (*a*) that both absorption bulbs are evacuated, (*b*) that a number of boats have been ignited for at least 24 hr. and allowed to cool in a desiccator, and (*c*) that the combustion tube has been at a temperature of 1100° C., with an oxygen flow of about 100 ml./min., for at least 20 min. The procedure is then as follows :

Weigh into one of the boats 2 g. of ether-washed sample, and place on top one piece of strip lead. The boats and lead should be handled with metal forceps and should be placed only on smooth clean carbon-free surfaces, such as silica or porcelain. The weighed samples are stored in a clean desiccator, preferably on a silica plate, until required.

Slowly lower one of the absorption tubes into liquid oxygen contained in a 1-pint vacuum flask, and connect the tube to the combustion apparatus, as shown in Fig. 1. Open tap *T*1 and tap *T*7, which controls the oxygen flow, until the absorption tube is full of oxygen. Then close *T*7 and open *T*2. Adjust *T*7 so that the rate of oxygen flow is about 60 ml./min., as indicated by the flowmeter. Remove the plug closing the combustion tube. This allows a rapid stream of oxygen to flow from the mouth of the tube, thus preventing ingress of air. With a pair of forceps place the boat and sample in the tube, push into position with a Nichrome probe, and replace the plug. The absorption tube is left in position for 20 min. to allow ample time for combustion of the sample and for isolation of all the carbon dioxide in the liquid-oxygen trap. The necessity for this time is shown by the following results on a sample containing 0·0477% of carbon :

Time for Combustion, min.	Carbon, %
10	0·0474
15	0·0479
20	0·0478
30	0·0478

Close taps *T*1 and *T*2 and disconnect the absorption tube. Transfer the tube, still in its bath of liquid oxygen, to the vacuum section, and connect it to the ground-glass joint *J*. Switch on the oil pump and open *T*4 and *T*2. This procedure roughly evacuates the absorption tube. While evacuation is proceeding, connect the other absorption tube to the combustion apparatus, and after removing the old sample, insert a fresh one and leave it to burn. By this time the rough evacuation of the first tube will be complete (test with a high-frequency spark tester). Close *T*4 and open *T*3 ; this will put the mercury vapour pump in circuit and in a few seconds all the residual oxygen in the tube will have been pumped into the Töpler system. Open *T*8 to air ; this will cause the mercury to rise in the Töpler bulb, trapping most of the gas present. Open *T*6 and *T*5 and momentarily reverse *T*8 ; this will clear *T*6 and *T*5 of any mercury blocking the keyway, thus allowing any water vapour present to be pumped out. Close tap *T*6 as the mercury passes it and reverse *T*8 to lower the mercury level again. Repeat the procedure, this time taking the mercury past *T*5. Close *T*5 and manipulate *T*8 to bring the mercury level to each of the calibration marks in turn, taking a pressure-reading at each stage. These readings are true zero readings. If the mercury is now lowered and a further sweep is carried out, the reading on the smallest bulb should be within 2 mm. of the true zero, confirming that the apparatus is completely evacuated.

Remove the flask of liquid oxygen from the absorption tube, and replace it with a beaker containing warm water to speed up the evaporation of the carbon dioxide. The complete evaporation of both carbon dioxide and the small amount of water present takes about 7 min. The carbon dioxide evolution is complete in 2–3 min., but the water in the tube is pumped off between the fifth and sixth minute. The apparatus can be left during this period while further samples are weighed or results are calculated. At the end of this time, a number of sweeps are made with the Töpler pump, the gas being collected in the calibrated volumes. Take readings for each sweep and continue

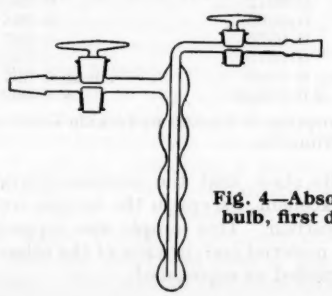


Fig. 4—Absorption bulb, first design

the sweeping until a constant reading is obtained, usually after the third sweep. The reading, temperature, and the particular calibration volume used are noted. Remove the absorption bulb from the apparatus by closing *T*3 and *T*2 and admitting air through *T*4 *via* a three-way tap connected in the vacuum line to ease the breaking of joint *J*. Place the tube in liquid oxygen, and about 2 min. will remain before the second carbon absorption tube is ready for treatment. Approximate timing of such a cycle is as follows :

0.00	Tube I connected to the combustion train
0.01	Gas flow adjusted, sample in
0.20	Tube I removed from the train, connected to the high-vacuum section, and rough pumping started
0.21	Tube II connected to the combustion train
0.22	Gas flow adjusted and sample in
0.23	*T*4 closed and *T*3 opened
0.24	Start sweeping with the Töpler pump
0.26	Zero reading taken, and the liquid oxygen replaced by warm water
0.33	Start sweeping with the Töpler pump
0.36	Final readings taken
0.37	Tube removed and placed in liquid oxygen
0.40	Tube II removed from the train and connected to the high-vacuum section, rough pumping started, and so on.

It will be seen from this time-table that one determination can be completed every 20 min. Blank determinations are carried out exactly as described above, using a boat and one strip of lead.

CALCULATIONS

With the foregoing procedure the carbon dioxide collected is always saturated with water vapour, presumably because of the low efficiency of the anhydrone as a dryer, compared with the liquid-oxygen trap. Correction for this water vapour can easily be made, by subtracting from the observed gas pressure the water vapour pressure at the temperature at which the reading was taken. Whilst the amount of water vapour could be reduced by passing the gas through a solid carbon dioxide trap before isolation of the carbon dioxide, this treatment may leave behind a small quantity of water which would defy correction. In addition, evidence is available to show that the water vapour actually aids the retention of the solid carbon dioxide in the trap.

Suppose that the zero-reading Z was obtained on a calibrated volume V with a final pressure-reading P at a temperature of $T°$ A. ; then

Wet gas pressure $= P - Z$
Let the water vapour pressure at $T°$ A. $= p$
$\therefore$ Corrected pressure $= P - Z - p$
Hence volume of gas at N.T.P.

$$= P - Z - p \times \frac{273}{T} \times V \text{ ml.}$$

Equivalent weight of carbon

$$= \frac{P - Z - p}{760} \times \frac{273}{T} \times \frac{V}{22{,}400} \times 12 \text{ g.}$$

The percentage of carbon present in the steel is therefore given by :

$$\frac{P - Z - p}{760} \times \frac{273}{T} \times \frac{V}{22{,}400} \times \frac{12}{\bar{2}} \times 100$$

The blank determination calculated in the same way should be subtracted from the figure obtained.

Reproducibility of the Method

The reproducibility of the method has been determined by analysing several standard steel samples six times, and the standard deviation has been calculated from the results. Only one in twenty results obtained will be outside the range given by $\pm 2S$. Results obtained by other methods on the same steel samples are also recorded below for comparison :

Carbon, %. Low-Pressure Method	Carbon, %. Other Methods
4% Silicon Steel	
0·0046	0·005*
0·0043	0·006*
0·0043	0·004*
0·0043	0·005*
0·0042	0·003*
0·0043	0·006*
Mean 0·0043	Mean 0·005
S 0·00014	*S* 0·0018
Plain Carbon Steel	
0·0101	0·009*
0·0106	0·012*
0·0103	0·011*
0·0104	0·010*
0·0105	0·009*
0·0104	0·010*
Mean 0·0104	Mean 0·010
S 0·00017	*S* 0·0018
Plain Carbon Steel	
0·0284	0·031*
0·0285	0·028*
0·0283	0·029*
0·0282	0·029*
0·0282	0·028*
0·0281	0·030*
Mean 0·0283	Mean 0·029
S 0·00015	*S* 0·0018
3% Silicon Steel	
0·0475	0·052†
0·0476	0·046†
0·0478	0·048†
0·0479	0·047†
0·0480	0·046†
0·0475	0·044†
Mean 0·0477	Mean 0·047
S 0·00022	*S* 0·003
Low-Alloy Steel	
0·0716	0·074†
0·0716	0·070†
0·0714	0·076†
0·0713	0·074†
0·0715	0·072†
0·0712	0·078†
Mean 0·0714	Mean 0·074
S 0·00017	*S* 0·003
Plain Carbon Steel	
0·0970	0·091†
0·0974	0·098†
0·0972	0·093†
0·0965	0·098†
0·0956	0·097†
0·0970	0·099†
Mean 0·0968	Mean 0·097
S 0·00065	*S* 0·003

* Absorption in barium hydroxide solution
† Gravimetric

The results show that the reproducibility of the method is excellent, except in the sample containing 0·097% of carbon. This sample was clipped from a sheet of the material and, in view of the other results, must be regarded as segregated.

Blank determinations made over a period of two or three months show that much of the variation observed must be due to variation in the blank :

Number of Determination	Carbon,%. Calculated on Basis of 2-g. Sample
1	0·0018
2	0·0015
3	0·0017
4	0·0017
5	0·0016
6	0·0015
7	0·0015
8	0·0017
9	0·0017
10	0·0014
11	0·0014
12	0·0015
Mean	0·0016
S	0·00015

Analysis of the blank has shown that it is made up as follows :

	Carbon, %
From the oxygen	0·00005
From the combustion boat	0·00035
From the lead strip	0·0012
Total	0·0016

The variation is most probably due to differences in the weights of the lead strip. A weight variation of ± 10% would give a blank range from about 0·0015 to 0·0017% of carbon, which agrees fairly well with the range observed. It would seem, therefore, that the reproducibility could be further improved by using a standard weight of lead, instead of the less precise method of cutting strips of roughly equal size.

Accuracy of the Method

There are usually two main procedures of computing the accuracy of a new method. One is to compare the results with those obtained by different methods. This has already been done and the foregoing results show a maximum difference of 0·003% of carbon for a sample containing 0·07% of carbon.

This agreement is contrary to the experience of Naughton and Uhlig,[9] who found that the standard method gave results which were approximately 0·004% too high. They ascribed this error to absorption of carbon dioxide by the alumina combustion boats when standing in air, and also to incomplete removal of sulphur dioxide from the gases formed during combustion.

These possible errors in the standard method were minimized in the results quoted, by careful blank determinations on the combustion boat and flux, and by the use of precipitated manganese dioxide for removal of sulphur dioxide. Neglect of these precautions will give results by the standard method which are about 0·005% too high.

This comparison is only a rough guide, since the potential accuracy of the two methods is so different. The other procedure involves estimation of the carbon content of material containing a known amount of carbon, usually a pure substance, for example, calcium carbonate. A micro-balance is required to obtain a sample weight of sufficient accuracy, and the fact that the substance used is not steel is a disadvantage. The method therefore tests only the accuracy of the means used to measure the amount of carbon dioxide formed, and does not test the combustion process.

It was considered that a better method would be to use a steel sample containing a relatively large amount of carbon, *e.g.*, 0·78%, and to determine the carbon content of small weights of the material. Assuming that the original carbon content was accurate to ± 0·01%, the real carbon figure would be in the range 0·77–0·79% of carbon. On a sample weight of, say, 0·0500 g., the carbon content calculated on a 2-g. basis should be between 0·01925 and 0·01975% of carbon. A result in this range could be considered satisfactory. The results of a number of determinations made along these lines were as follows :

Weight of Sample, g.	Carbon Present on 2-g. Basis, %	Carbon Determined on 2-g. Basis, %	Carbon Determined on True Weight Basis, %
0·2000	0·0780 ± 0·001	0·0784	0·784
0·1000	0·0390 ± 0·0005	0·0388	0·776
0·0500	0·0195 ± 0·00025	0·0196	0·784
0·0200	0·0078 ± 0·0001	0·0078	0·78

These figures show that the accuracy of the method compares favourably with the reproducibility, the results being well within the range of known sample composition.

This method of carbon determination could also be used for the micro-determination of carbon in steel, using sample weights as low as 0·02 g. For this purpose the apparatus could be modified, by scaling down in size, to give even more accurate results.

LIQUID OXYGEN SUPPLIES

The liquid oxygen is supplied in 1-gal. containers which can be refilled, and is transferred from the container to the 1-pint vacuum flasks when necessary. Under normal conditions the large container requires filling every week.

Acknowledgments

The author is indebted to Mr. H. H. Stanley, Chief Metallurgist of The Steel Company of Wales (Lysaght Works), Ltd., for continued interest and encouragement during the construction of the apparatus, and to the Directors of that Company for permission to publish this paper.

References

1. T. D. YENSEN : *Transactions of the Electrochemical Society*, 1920, vol. 37, p. 227.
2. N. A. ZIEGLER : *Ibid.*, 1929, vol. 56, p. 231.
3. L. A. WOOTEN and W. G. GULDNER : *Industrial and Engineering Chemistry* (*Analytical Edition*), 1942, vol. 14, p. 835.
4. W. M. MURRAY and S. E. Q. ASHLEY : *Ibid.*, 1944, vol. 16, p. 242.
5. J. K. STANLEY and T. D. YENSEN : *Ibid.*, 1945, vol. 17, p. 699.
6. M. H. KALINA and T. L. JOSEPH : *Heat Treating and Forging*, 1939, vol. 25, p. 169.
7. C. E. NESBITT and J. HENDERSON : *Industrial and Engineering Chemistry* (*Analytical Edition*), 1947, vol. 19, p. 401.
8. G. ERICSSON : *Jernkontorets Annaler*, 1944, vol. 128, p. 579.
9. J. J. NAUGHTON and H. H. UHLIG : *Analytical Chemistry*, 1948, vol. 20, p. 477.

Rapid Estimation of Phosphorus in Steels

By A. Hans

SYNOPSIS

Following a short outline of the methods of Hanau and Wolfe and of Hasler and Barley, for the spectrographic determination of steel, the results of a number of comparative experiments made with these methods are given.

These experiments induced the author to study two types of receiver, namely, the Geiger-Müller counter and the electron multiplier tube, and to compare their respective values for use in the estimation of phosphorus. These researches bore also upon the conditions of excitation, and the one definitely favoured is a special arc-discharge, which markedly weakens the line in the neighbourhood of the 2149 P line. The standard deviation is about 2·5% and the analysis time is about 50 sec.

Introduction

THE determination of phosphorus in steel by spectrographic methods is subject to difficulties since the phosphorus lines most suitable for the analysis of low-phosphorus materials (containing 0·005–0·01%) are interfered with by the neighbouring iron lines (neighbourhood of 2500 Å.) or have relatively short wavelengths (about 2100 Å.); they are therefore strongly absorbed in the gelatine of the photographic emulsion. The extreme phosphorus line is in the region of 1700 Å. Unfortunately, this line is absorbed by air, and it is necessary to work in a vacuum or in a nitrogen atmosphere. It is obvious that such a method is hardly suitable for industrial use.

Different workers have attacked the problem of phosphorus estimation in steels, and amongst the suggested methods those of Wolfe and Hanau, and of Hasler and Barley will be very briefly summarized:

In 1947, Wolfe and Hanau made use of a method at the University of Michigan[1] which is now in use at the Ford Motor Company[2] (Dearborn, Michigan). The 2136 Å. arc phosphorus line was selected, being sufficiently sensitive and offering least difficulty of resolution, although it is about 0·2 Å. from a strong line in the spark spectrum of copper.

To separate the two lines, they used a Littrow spectrometer with a high dispersion (1·7 Å. per mm. in the neighbourhood of 2100 Å.), the luminosity of which is about four times smaller than that of a quartz spectrograph of medium dispersion.

The large dispersion given by the Littrow permits the use of very wide exit slits (of the order of 200μ), thus reducing errors due to the movement of the luminous source, and to variations of the ambient temperature.

To measure the intensity of the phosphorus line and the iron line, the authors used Geiger-Müller counters instead of electron multiplier cells. In this connection, attention should be drawn to the following points:

(*a*) Electron multiplier cells cannot detect a signal when its intensity is below a certain minimum. Geiger-Müller counters, on the other hand, are not subject to any such limit; however weak the signal, it can be separated from the background noise by using a sufficiently long exposure period. This is a point in favour of counters when weak radiations are to be measured.

(*b*) The sensitivity of Geiger-Müller counters increases towards short wavelengths (2000 to 2500 Å.) The limit of sensitivity is about 3000 Å.

To make clear this variation in sensitivity, a brief account of the operation of a counter is given below.

In principle, the counter consists of a cylinder (serving as cathode), along the axis of which lies a tungsten wire (the anode). Between the cylinder and the central wire a potential difference of the order of 1000 V. is set up, and the whole is enclosed in an envelope which transmits ultra-violet light, and is filled with gas under reduced pressure.

Any photon with energy $h\nu$* which enters through a window cut in the cathode will release an electron from the inner surface of the cylinder if its energy is greater than or equal to the work function A of the metal; in other words, the wavelength of the incident radiation must be less than a certain value λ_A. The electron released from the metal, known as a photo-electron, is accelerated by the electric field between the cylinder and the filament; it ionizes the gas and sets free a burst of secondary electrons which move towards the central filament. An electronic measuring system counts the number of bursts or discharges, *i.e.*, the intensity received by the counter.

The advantage of Geiger-Müller counters in the short-wave region is their insensitivity to diffused light of wavelength greater than λ_A; this means that the ratio of the intensity of a line to the intensity of the continuous background is greater than in the case of electron multiplier cells.

Using an alternating-current arc as source (1·7 amp. at 4400 V., or 3·5 amp. at 2200 V.) and two metal electrodes as samples, Wolfe and Hanau estimated phosphorus with a standard deviation of the order of 10%. The time required for an analysis was of the order of one minute.

Hasler and Barley[3] have quite a different analytical technique. They used Radio Corporation of America

Manuscript received 28th December, 1949.

Mr. Hans is a member of the staff of the Centre National de Recherches Métallurgiques (Liège).

* h is Planck's constant, ν the frequency of the radiation.

cells, type 1*P*28, selected for their sensitivity in the region of 2100 Å. They used the first-order spectrum of a spectrograph with a concave grating of 2 m. focal length, giving a dispersion of 5 Å. per mm. The luminosity of this spectrograph at short wavelengths is as great as, if not greater than, that of a quartz spectrograph of medium dispersion.

To avoid the disadvantage of a very narrow exit slit, the authors proposed to measure the copper and phosphorus intensities simultaneously by means of a wide slit, and to estimate the copper later from an entirely different line, thus finding the phosphorus content by difference. If, in a preliminary experiment, the relation between the intensity of the single copper line and the overlapping copper and phosphorus lines has been determined, the readings are obtained directly. They used the phosphorus line 2149·1 which overlaps the copper line 2148·9.*

The copper was determined by the 3273·9 line. They used the simple technique of the flat sample. The counter electrode is of graphite and the excitation conditions are those of an arc fed by a multisource. The standard deviation obtained by this method is about 7%.

It was the present author's intention to compare these two techniques and to find whether Geiger-Müller counters are superior to electron multiplier cells when used at short wavelengths. Further, an investigation of the 2500 Å. region, where all 1*P*28 photo-tubes are very sensitive, was to be made; in this region the interfering element does not arise. Lastly, the 2100 Å. region was used with special excitation conditions which greatly reduced the intensity of the copper line.

The experimental programme led to numerous researches, which will be divided into three classes, according to the receivers used.

* The authors preferred the 2149·1 line to the 2136·2 line because the interfering copper line is much weaker.

ELECTRON MULTIPLIER CELLS

A tube fairly sensitive in the 2100 Å. region was chosen,[4] and an apparatus manufactured by the Applied Research Laboratories, Glendale, California, was used, with the technique suggested by Hasler and Barley. The author's direct-analysis apparatus[5] functions as follows.

A series of semi-mobile slits situated on the Rowland circle isolates from the spectrum rays about 100μ wide. The light traversing these slits is reflected through 90° either upwards or downwards by means of small cylindrical concave mirrors (4·8 mm. wide), and then falls on a photocell which incorporates an electron multiplier (Fig. 1.) The currents generated by the photocells each charge up a condenser of high dielectric resistance, the potential across which is measured by a very high impedance bridge amplifier of the Wynn-Williams type,† and a rapid potentiometric recorder (Leeds and Northrup Speedomax).

If V_F is the potential across the condenser corresponding to the basic element, and V_A is that corresponding to the line from an additional element, the ratio V_A/V_F is a measure of the ratio of the intensities of the two rays under consideration, and is therefore a measure of the concentration of the additional element in the basic element.

To simplify matters, an arbitrary fixed charge is given to the condenser corresponding to the basic element, and the potentials of the condensers corresponding to the additional elements are measured. This simplification is obtained in practice by following, during the sparking period, the increase in potential of the condenser corresponding to the main element.

† When the grid potential of one of the pentodes alters, the dynamic equilibrium of the bridge is upset and the change is recorded. Note that, since the potentials are measured by a grid, the condensers are not discharged. This ensures accuracy and enables repeat measurements to be made.

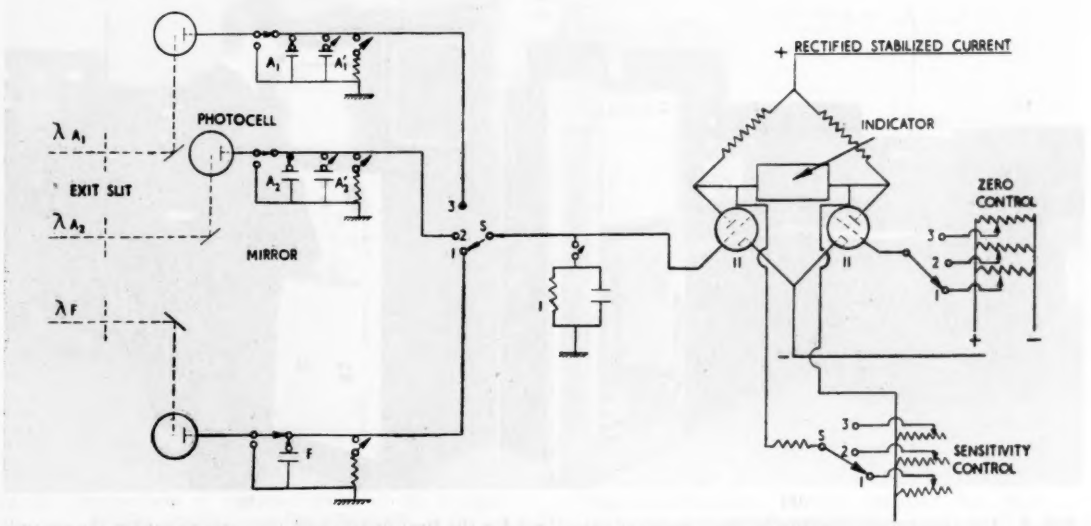


Fig. 1—Circuit of the electronic part of the apparatus

Table I

ESTIMATION OF PHOSPHORUS IN STEELS

(1) Sample	(2) Cu, % (3274 Å.)	(3) P, % (2149·10 Å.)	(4) P, % (2553·28 Å.)	(5) P, % (2535·65 Å.)	(6) P, % (Obtained Chemically)
1	0·090	0·020	0·015	0·023	0·019
2	0·045	0·042	0·033	0·038	0·033
3	0·040	0·090	0·080	0·093	0·099
4	0·030	0·045	0·050	0·038	0·044
5	0·035	0·060	0·055	0·061	0·057
6	0·030	0·045	0·040	0·048	0·045
7	0·045	0·060	0·063	0·068	0·062
8	0·090	0·020	0·025	0·013	0·019
9	0·040	0·055	0·050	0·059	0·054
10	...	...	0·085	0·078	0·080

As soon as this condenser reaches the standard value, a cut-out, placed on the recorder itself, automatically cuts off the current to the light source, and in consequence stops simultaneously the charging-up of all the condensers. It is therefore sufficient to measure the potentials of the additional condensers by connecting them in turn to the grid of the pentode 1, by means of a rotary switch *S*.

To facilitate the establishment of scales of concentration, an apparatus was introduced to control the potential of the second pentode of the bridge. A second control regulates the current through the recorder and, in consequence, adjusts its sensitivity. These two controls enable one to operate in the optimum region of the scale of concentrations, and to increase its sensitivity to the maximum.

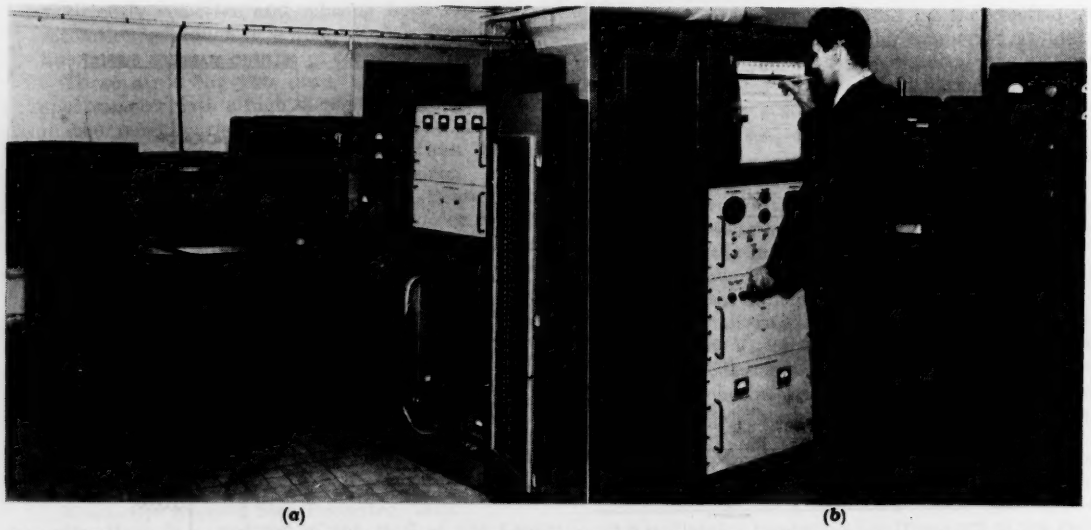
In addition, the circuits corresponding to each of the additional elements are provided with two condensers of equal capacity which can be introduced alternatively into the circuits. By this means, the instrument can be rapidly calibrated by storing in one of the condensers the charge due to a standard sample with a low content of the element under investigation, and in the other condenser the charge due to a standard sample with a high content of the element. By connecting each of these two condensers in turn to the amplifier, and using the zero and sensitivity controls, any desired scale of concentration can be selected.

Column (3) of Table I gives the results obtained when estimating the phosphorus in nine samples of steel. The standard deviation* is of the order of 7%, which confirms the results of Hasler and Barley.

Figure 2 is a general view of the author's apparatus, in which the multisource and the electronic measuring system can be seen.

The time taken for an analysis is 60 sec., including preparation of the specimen, which in the author's case consists simply of grinding.

* Obtained from 40 determinations on the same sample.



(*a*) (*b*)

Fig. 2—The apparatus, showing (*a*) the " receiver case " set for the first order, and the camera set for the second; (*b*) the recording potentiometer

Although Hasler and Barley's solution is very elegant, it unfortunately necessitates a photo-cell which is sensitive in the short-wavelength region. To avoid this disadvantage, the author undertook an investigation of the 2500 Å. region, in which are found two phosphorus lines : 2535·6 and 2553·3.

The arc line 2535·6 is by far the more sensitive. It is interfered with by a line in the iron arc at 2535·6 and by a line in the iron spark spectrum of wavelength 2535·5 Å.

By using the second order of the instrument, the dispersion is sufficient to separate the spark line from the two arc lines of phosphorus and iron. Despite the superposition of the iron arc line, the sensitivity was both relatively and absolutely superior to that obtained with the 2149·1 Å. line. The standard deviation in this case is of the order of 6%. The difference is certainly not large, but it is nevertheless significant, since the author's experiments were carried out using simultaneously the phosphorus lines at 2149·1 and 2535·6 Å.

The 2553·3 line (*see* column (4) of Table I) was also used. The sensitivity for this line is not great enough to detect less than 0·01% of phosphorus, and the standard deviation obtained was greater than 7%.

The next question was whether it was possible to improve the performance with the 2149·1 line by using a special discharge which would have the properties of :

(1) Considerably reducing the intensity of the interfering copper line, which belongs to the spark spectrum, whereas the phosphorus line belongs to the arc spectrum

(2) Reducing as much as possible the effects of segregation. The surface on which the arcs play is comparatively small, which makes the results obtained very sensitive to small segregations, and still more so to large ones

(3) Reducing the effects of movements of the arc.

To satisfy these conditions, use was made of a high-intensity unidirectional intermittent arc, operating with a gap of 5 mm. between the electrodes, and supplied from an Applied Research Laboratories multisource.

The impact surface of this discharge is far greater than that previously obtained. The ratio between the diameters is about four to one. With this discharge the error was of the order of 5%. The time required for an analysis was still small, about 55 sec.

GEIGER-MÜLLER COUNTER AND ELECTRON-MULTIPLIER CELL

Since it did not appear that the sensitivity of photocells was sufficiently great, a Geiger-Müller counter was used for the 2100 Å. region, a photocell being still used for the reference line in the iron spectrum.

Under these conditions, the luminous source is cut off as soon as the iron-line condenser has acquired the standard charge. Then the desired concentration is read off from the number of impulses shown on the dial of the electromagnetic clock which is coupled to the Geiger counter.

To investigate the difference in sensitivity between photocells and Geiger-Müller counters at short wave-

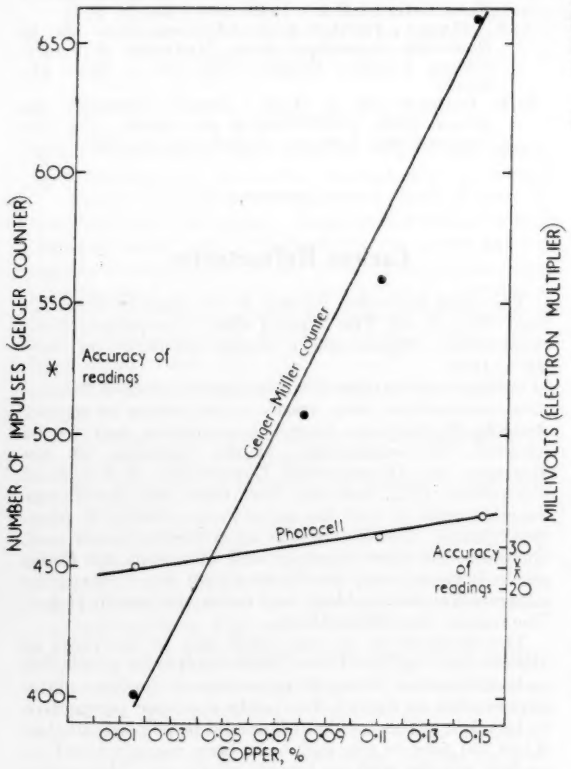


Fig. 3—Comparison of the sensitivity of the Geiger-Müller counter and the photocell

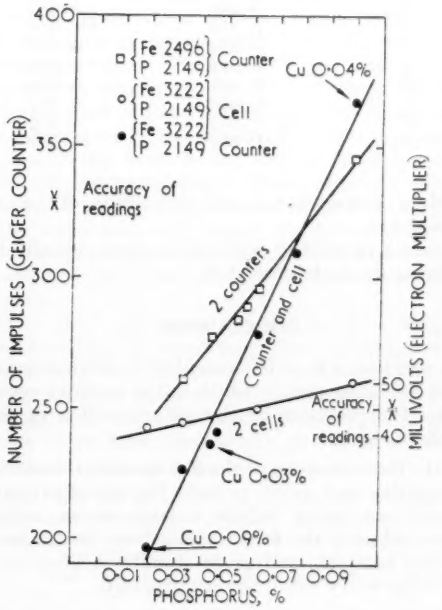


Fig. 4—Calibration curves obtained by the three methods

lengths, the copper was first estimated by means of the spark line at 2148·9 Å. For that it was sufficient to use a spark to excite the copper line and completely to suppress the phosphorus line. The conditions were therefore excellent for comparing the two receivers solely from the electronic point of view. Figure 3 shows two curves, one obtained with the photocell, the other with a counter. This comparision was repeated on different days, and showed that the Geiger counter was very sensitive and accurate.

The special excitation condition was then used to estimate the phosphorus. The standard deviation obtained with this combination of methods is of the order of 3%.

TWO GEIGER-MÜLLER COUNTERS

There remained one last possibility: the use of two Geiger-Müller counters.

The following lines were used: phosphorus 2149·1 Å. and iron 2496·9 Å. The recording was stopped when the dial corresponding to the counters operated by the iron line showed a fixed number of impulses.*

The standard deviation was about 2·5% under the special conditions of excitation. The results of some estimations made by this method and with samples of plain carbon (basic Bessemer) steel are given below:

Estimation of Phosphorus in Steels by Means of Two Geiger-Müller Counters

Sample	P, % (2149·10 Å.)	P, % (Obtained Chemically)
1	0·100	0·104
2	0·085	0·084
3	0·070	0·073
4	0·070	0·066
5	0·062	0·064
6	0·065	0·061
7	0·050	0·050
8	0·034	0·033
9	0·047	0·044
10	0·051	0·054
11	0·056	0·057
12	0·062	0·062
13	0·101	0·099

The time of analysis was still very short, of the order of 50–55 sec.

Figure 4 shows the calibration curves obtained by the three methods described.

CONCLUSION

In conclusion it is felt essential to draw attention to the following points, which in the author's opinion control the precision of the determination of phosphorus in steel:

(1) The technique of the flat specimen, besides its simplicity and speed, permits the use of excitation conditions which induce a large arcing surface, thus reducing the error arising from heterogeneity of the samples, and gives a uniform illumination over the entry slit of the spectrograph.

(2) The use of sufficiently wide exit slits considerably reduces errors due to displacement of the spectrum.

(3) If the 2149·1 Å. phosphorus line is used, it is necessary to weaken the interfering copper line by selecting special excitation conditions.

(4) Geiger-Müller counters have the advantage of greater sensitivity over photocells and at short wavelengths.

The method is applicable to all dispersive systems, whether they depend on a prism or on a grating. The choice depends in the first place on the analysis programmes of the laboratories, and the different methods must be examined in each particular case; in any case it is desirable to take care of the future by choosing an apparatus with the greatest possibilities.

Acknowledgments

This research was carried out under the auspices of the Institut pour l'Encouragement de la Recherche Scientifique dans l' Industrie et l'Agriculture.

References

1. R. HANAU and R. A. WOLFE: *Journal of the Optical Society of America*, 1948, vol. 38, Apr., pp. 377–383.
2. F. R. BRYAN and G. A. NAHSTOLL: *Journal of the Optical Society of America*, 1948, vol. 38, June, pp. 510–517.
3. M. F. HASLER and F. BARLEY: *Spectrographer's News Letter* (*A.R.L.*), 1949, Sept., No. 14, p. 1.
4. A. HANS: *Institut pour l'Encouragement de la Recherche Scientifique dans l'Industrie et l'Agriculture, Comptes Rendus*, 1949, No. 1, Nov., pp. 79–95.
5. P. COHEUR and A. HANS: *Revue Universelle des Mines*, 1949, vol. 5. No. 2, pp. 63–68. *See The Iron and Steel Institute, Translation No.* 378.

* This is, in effect, the equivalent of the quantometer system.

Carbon Refractories

The third all-carbon furnace at the Appleby-Frodingham Branch of The United Steel Companies, Ltd., Scunthorpe, experienced a hearth breakout on July 24th, 1950.

Owing to limitations of site and peculiarites of foundation construction, very drastic modifications to regular Appleby-Frodingham hearth construction had to be adopted. Full examination of the breakout, by the Research and Development Department of The Steel Companies, Ltd., indicates that there was insufficient hearth carbon to chill the metal known always to penetrate joints. Because of the short hearth jacket and, therefore, the short chimney wall, this iron, still liquid at the bottom of the hearth, found its way through the concrete foundation block and under the hearth jacket. The furnace was off for 38 hrs.

This breakout in no way alters any of the views or theories held by The United Steel Companies in relation to hearth carbon; if anything it enhances the value of the experiments in hand. To enable a proper perspective to be taken of this breakout it should be pointed out that 2,910,920 tons of pig iron have been manufactured on carbon hearths with no trouble whatever. The corresponding tonnage of iron made before the introduction of carbon was accompanied by 14 breakouts.

B. I. S. R. A.

BRITISH IRON AND STEEL RESEARCH ASSOCIATION

Corrosion of Bare Iron or Steel in Sea Water

By J. C. Hudson, D.Sc., F.I.M.

SYNOPSIS

The results so far obtained in the course of the Corrosion Committee's work relating to the corrosion of structural irons and steels when immersed in sea water are presented and critically examined.

The presence of millscale on the iron or steel is shown to promote serious pitting in sea water. The rate of general corrosion of mild steel when immersed in British waters after removal of the millscale is found to be approx. 3–5 mils/yr. There is little, if any, difference in the corrosion rates, under these conditions, of ordinary unalloyed ferrous materials, such as mild steel, ingot iron, or wrought iron.

Of a wide range of alloying elements incorporated in a series of low-alloy steels, only two, chromium and nickel, are shown to have any significant effect in reducing the corrosion rate. Steels containing 2–3% of chromium were found to corrode at one-half or one-third of the rate of unalloyed steels of the same carbon content. The effect of nickel additions was less marked.

No significant difference has been observed in the behaviour of ordinary and of copper-bearing steels when totally immersed in sea water.

Introduction

THE corrosion of bare iron or steel when totally immersed in sea water without any protection has been investigated in several series of tests by the Corrosion Committee. Some of the earlier results obtained have been published but no report has yet appeared on the most recent work. The present paper reviews the Committee's researches in an endeavour to show what facts may now be regarded as established and to indicate what direction further experimental work should take.

The subjects considered in relation to corrosion in sea water are :

(1) The effect of the conditions of immersion
(2) The effect of millscale
(3) The rate of corrosion of ordinary mild steel in sea water
(4) The effects of differences in the composition of iron or steel on the rate of corrosion. The experimental work under this head has, however, been limited to ordinary or low-alloy structural materials, as distinct from high-alloy steels.

EFFECT OF THE CONDITIONS OF IMMERSION

The effect of the conditions of immersion was studied in the first series of tests in this field which were begun at Gosport in September, 1935. Theoretically, corrosion should be controlled by the rate of supply of oxygen to the steel surface, which might be expected to decrease with the depth of immersion. The tests were, therefore, designed to study this variable. Four sets of four 15-in. × 10-in. × $\frac{3}{8}$-in. specimens of the same steel were exposed at four different depths on a wooden frame fixed beneath the pontoons of the Gosport landing stage.* The specimens were in the as-rolled condition and were arranged in four rows, the first of which broke the surface of the water. The depths of immersion of the other three rows, measured to the top edges of the specimens were 5, 23, and 41 in. respectively. When they were taken out from the water after six months, those in the top row, which had been exposed at the water line, were rusted and blistered but were free from marine growth. There was a copious marine growth on the specimens that had been totally immersed.

After they had been cleaned by scrubbing and wire-brushing, the specimens were re-weighed and examined in the laboratory. The totally immersed specimens had retained most of their millscale. Rusting had been confined to about 15% of the surface ; over these areas severe pitting up to 0·05 in.

Paper MG/BD/49/49 of the Industrial Waters (Corrosion) Sub-Committee of the Metallurgy (General) Division of the British Iron and Steel Research Association, received 17th February, 1950. The views expressed are the author's and are not necessarily endorsed by the Sub-Committee as a body.

Dr. Hudson is Head of the Association's Corrosion Laboratory, Birmingham.

* With the collaboration of the Borough Engineer and Surveyor, Mr. A. Barlow, A.M.I.C.E.

Table I

EFFECT OF DEPTH OF IMMERSION ON THE RATE OF CORROSION OF MILD STEEL

Depth of Immersion, in.*	Loss in Weight, oz./specimen†	Area Corroded, sq. ft.	Rate of Corrosion over the Corroded Area	
			oz./sq. ft./yr.	mils/yr.
−12‡	0·4	0·91	1	1
5	4·8	0·35	28	42
23	4·2	0·32	26	40
41	3·9	0·29	28	42

* Measured to the top (10 in.) edge of the specimens.
† The area of a specimen was 2·23 sq. ft. and the duration of immersion 0·5 yr.
‡ Only the lowest 3 in. of the specimens were immersed.

deep had occurred. Most of the millscale was covered with a thin white deposit, which could not be removed with a scrubbing brush. This deposit probably consisted of calcium and magnesium salts precipitated from the sea water (*see* p. 126). It was impracticable to derust the specimens in an acid bath owing to the presence of millscale, but the losses in weight were determined after the rusted areas had been cleaned as much as possible by wire-brushing.

The results given in Table I show that the rate of rusting is less for specimens exposed at the water line than for totally immersed specimens, and that in the latter case the rate decreased with increasing depth of immersion. For the standard 15-in. × 10-in. specimens used in the bulk of the Committee's tests, the conditions of exposure were sufficiently uniform at depths below 14 in. measured to the top 10-in. edge.

EFFECT OF MILLSCALE

If the total corrosion of the specimens in the test described above is divided by the estimated percentage area over which rusting had occurred, figures are obtained for the rate of attack at the areas free from millscale (*see* Table I), and lead to the conclusion that the presence of millscale on steel immersed in sea water engenders dangerous localized corrosion. The average rate of attack on the rusted areas ranged up to 42 mils/yr., but the maximum rate of pitting reached 100 mils/yr. This intensification of the rate of attack is caused by electrochemical action between the millscale and the bare metal, which results in a concentration of the attack at areas where the millscale is damaged or absent. Comparative tests of the resistance of different materials to rusting in sea water will therefore be valid only if they are made on descaled specimens. If the specimens are not descaled the results of the tests may merely reflect differences in the character and state of repair of the respective millscales at the time of exposure and may not be representative of the materials themselves.

RATE OF CORROSION OF ORDINARY MILD STEEL

Observed values for the rates of corrosion of ordinary 0·2% carbon steel when immersed in sea water off the coast of England and Wales are given in Table II. The specimens, of various sizes, were descaled and immersed for periods of up to four years at depths of 1–3 ft.

The rate of corrosion varied from about 3–8 mils/yr., according to the test conditions. For standard-size specimens, a value of 3–5 mils/yr. may be taken as representative. This is about the same rate as that observed for the corrosion of this type of steel in a heavily polluted industrial atmosphere. In both cases the figure applies to general corrosion and takes no account of pitting. Generally, however, pitting is not appreciable on specimens exposed without millscale.

The rate of corrosion appears to vary with the specimen size. For example, in a series of tests made simultaneously at Plymouth, on mild steels of similar composition, although not from identical casts, the rates observed for 15-in. × 10-in. × $\frac{3}{8}$-in., 8-in. × 8-in. × $\frac{1}{4}$-in., and 6-in. × 4-in. × $\frac{1}{4}$-in. specimens were 4·5, 6·0, and 7·9 mils/yr., respectively. The effect of different dimensions may be attributed to the fact that the cut edges of the specimens probably corrode more rapidly than the rolled surfaces. It can be calculated from results obtained in the B.I.S.R.A. Corrosion Laboratory that, if two 6-in. × 4-in. specimens of ordinary steel, $\frac{1}{8}$ in. thick in one case and $\frac{1}{2}$ in. thick in the other, were immersed in 7·5N sulphuric acid at 40° C., the amount of steel dissolved per unit area would be 35% greater in the case of the thicker specimens, because the rate of solution from the cut edges was 4·5 times greater than that from the faces. Admittedly, pickling in acid is not identical with immersion in sea water, but the same considerations probably apply to some extent. In general, therefore, it seems desirable to use fairly large specimens for marine corrosion tests whenever possible. If smaller specimens must be used, the ratio of total surface area to the area of the cut edges should be as high as possible and the same for all specimens.

EFFECT OF COMPOSITION OF THE MATERIAL

General Remarks

The effect of differences in composition on the rates of corrosion of iron or steel immersed in sea water has been studied in four series of tests, brief particulars of which are given in Table III.

The specimens were attached to exposure frames totally immersed in the sea in a vertical position at depths of approx. 2–3 ft. In all cases direct metallic contact between the specimen, the frame, and the fixing bolts was avoided by the use of suitable plastic washers and bushes. Apart from any effects of tide and current, the specimens were at rest in relation

Table II

RATE OF CORROSION OF TOTALLY IMMERSED 0·2% CARBON STEEL

Locality	Duration	Size of Specimen, in.	Corrosion Rate, mils/yr.
Gosport	1·2 yr.	15 × 10 × $\frac{3}{8}$	4·9
Plymouth	29 wk.	15 × 10 × $\frac{3}{8}$	4·5
		8 × 8 × $\frac{1}{4}$	6·0
		6 × 4 × $\frac{1}{4}$	7·9
Caernarvon	26 wk.	15 × 10 × $\frac{3}{8}$	4·4
Caernarvon	52 wk.	15 × 10 × $\frac{3}{8}$	4·3
Emsworth	4 yr.	15 × 10 × $\frac{3}{8}$	2·6
Emsworth	2 yr.	3 × 2$\frac{1}{2}$ × $\frac{1}{8}$	2·7

to the water. As a result, their surfaces rapidly became fouled with marine organisms, as shown in Fig. 1. Where the specimens had been exposed for long periods, the fouling and the subjacent layer of rust were extremely difficult to remove. In the series of tests in which specimens were immersed at Emsworth for four years, it was found necessary to wire-brush them after the conclusion of immersion, immerse them for 20 min. in cold dilute sulphuric acid containing an inhibitor, and heat the surfaces with a Bunsen flame. This caused much of the rusty scale to flake off. The specimens were then scraped and immersed again in the cold dilute sulphuric acid for about 1–1½ hr. Finally, derusting was completed by treatment with Clarke's solution for 1½ hr.

Effect of Exposure Conditions—As rusting is essentially controlled by the access of oxygen to the steel surface, a number of different irons and steels immersed in sea water will all corrode at the same rate, unless the rate of oxygen supply is at least greater than that required for the maximum corrosion rate that is possible under the given conditions for the most resistant member of the group. Moreover, the maximum differences between the least and the most corroded materials will only develop if the rate of oxygen supply equals or exceeds that at which the corrosion process of the least resistant iron or steel is capable of using up oxygen. In the case of specimens exposed under the static conditions, there is probably considerable interference with the access of oxygen to the metal, because of (*a*) the accumulation of rust on the surface, (*b*) the deposition of calcium and magnesium compounds from the sea water as a result of the corrosion process, and (*c*) the outer layer of fouling organisms. The fact that the rust beneath the marine growth is often found to be black indicates that it is not completely oxidized and it may be that

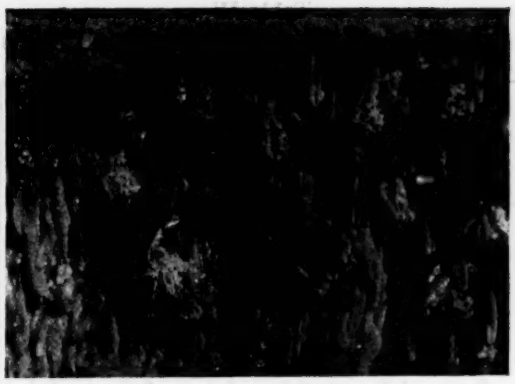


Fig. 1—Fouling of specimen after immersion at Gosport for 1·2 yr.

in some cases anaerobic conditions prevail at the steel surface. Whether this is so or not, under conditions of static immersion there will be a tendency for the corrosion rates of all irons and steels, except perhaps those of the rust-resisting steels proper, to become reduced to the same figure. If the marine growth is not disturbed, this rate might be expected to become slow after several years' immersion.

It is of interest to consider the other case—so far as the Committee's researches to date are concerned, a purely hypothetical one—in which the specimens are immersed in the sea but move through it at such a rate that they do not foul. These conditions would correspond to those to which a bare plate on a ship's bottom would be exposed, when in rapid motion away from port ; steel or iron built into the underwater structure of a pier or jetty is more adequately

Table III

CORROSION COMMITTEE'S TESTS

Locality	Date	Duration of of Test	Materials Tested	Size of Specimen, in.
Gosport	1937–38	1·2 yr.	Scottish wrought iron *V* Ingot iron *W* Mild steel *X* Mild steel, Cu 0·5%	15 × 10 × ⅜
Plymouth	1940	7 months	9 mild steels, 6 copper-bearing steels, and 5 chromium–copper steels 3 aluminium–chromium steels Ingot iron *W*, mild steel (ship-plate quality), 'D' steel, and 4 low-alloy steels	8 × 8 × ⅛ 6 × 4 × ⅛ 6 × 4 × ⅛ to ½*
Emsworth	1944–48	4 yr.	Staffordshire wrought iron *T* Ingot iron *W* Mild steel *X* 'D' steel and 4 low-alloy steels	15 × 10 × ⅜ or ½
Emsworth	1946–48	2 yr.	57 mild steels or low-alloy steels, prepared as laboratory heats	3 × 2½ × ⅛

* The thickness varied for different materials from ⅛ in. to ½ in.

Table IV

CORROSION RATES OF IRONS AND STEELS (GOSPORT TESTS)

Frame No.	Loss in Weight, oz./specimen*				
	Scottish Wrought Iron *V*	Ingot Iron *W*	Mild Steel *X*	Copper-bearing Steel *Z*	Average
1	7·4	8·9	8·3	8·7	8·4
2	7·7	9·2	8·1	9·2	8·6
3	7·0	8·9	8·4	8·1	8·1
4	7·8	8·5	8·9	9·1	8·6
5	7·5	9·1	9·2	9·5	8·8
6	7·6	9·3	8·9	9·1	8·7
7	7·1	8·9	8·9	9·0	8·5
8	7·2	9·2	9·0	8·8	8·5
9	6·9	8·8	8·4	8·9	8·3
10	8·0	8·6	8·4	8·1	8·3
Average	7·4	8·9	8·7	8·9	8·5

* Mean values for duplicate specimens. The period of immersion was 1·21 yr. and the surface area of a specimen was 2·23 sq. ft.

represented by static specimens. It is probable that, if the motion were sufficient to prevent the settlement of fouling, the adhesion of rust to the surface would also be reduced. Consequently, there should be much less interference with the access of oxygen to the steel and, so far as this factor is concerned, there should be an opportunity for any differences in the corrosion resistance of, say, a range of low-alloy steels to come into play. On the other hand, so far as is known, it is precisely the differences in the various types of surface rust formed on different types of ordinary or low-alloy steels that are responsible for the marked differences in the resistance of these materials to atmospheric attack. The effect of motion through the water may prevent any accumulation of surface rust and thus render it impossible for this factor to become operative.

Therefore, neither under stagnant conditions nor under conditions of rapid movement through the water are marked differences in the resistance of ordinary ferrous materials, including low-alloy steels, towards attack by sea water to be expected. Highly alloyed rust-resisting steels, which depend for their immunity from corrosion on the presence of an intact oxide film on their surface are excluded. The conditions under which marine corrosion tests are conducted will have a marked effect on the results. The rates of rusting given relate to static specimens and may not apply to specimens in motion.

Significance of Results—The second important factor to be kept in mind when considering the results is the degree of reliability or significance of the figures obtained for the rates of corrosion. The reproducibility of the results for duplicate specimens is on the whole less good for marine immersion tests than for atmospheric exposure tests ; in the second series of tests at Emsworth (*see* p. 130), the percentage difference between duplicate specimens ranged from 0·2 to 87 ; the average value for 58 steels was about 17%. The corresponding average for 417 pairs of specimens exposed in the Committee's atmospheric corrosion tests is about 2%. Little significance should therefore be attached to differences between different materials amounting to less than about 20%. Where appropriate, simple statistical tests are applied to check the significance of the results.

Tests at Gosport

The effect of the position of the exposure frame beneath the landing stage at Gosport on the corrosion of the specimens was investigated in some early tests. Ten frames, holding eight standard specimens, 15 in. × 10 in. × $\frac{3}{8}$ in. in two rows of four, were fixed in positions distributed as uniformly as possible under the landing stage. Each frame carried duplicate specimens of four different materials, steel *X*, Scottish wrought iron *V*, ingot iron *W*, and copper-bearing steel *Z* (Cu 0·5%) ;* all the specimens were sand-blasted and one specimen of each material was placed in each row.

The specimens were immersed for 1·2 yr., from February, 1937, to May, 1938. When they were removed, they were found to be heavily covered with marine growth, as shown in Fig. 1. The rust beneath the marine growth was black, *i.e.*, it had not completely oxidized to ferric hydroxide. Over large areas a white calcareous deposit was found in direct contact with the metal which seemed to have partially protected it. An analysis† of this white deposit, which consists essentially of calcium carbonate, is as follows : calcium carbonate, 57% ; calcium sulphate, 3% ; ferric oxide, 19% ; magnesium carbonate, 3% ; sodium bicarbonate, 5% ; insoluble siliceous matter, 8% ; water and other constituents (by difference), 5%. The probable explanation of the formation of this white deposit is that conditions near the non-corroded cathodic areas become more alkaline, and this depresses the solubility of the calcium and magnesium compounds present in the sea water, with the result that they are precipitated on the surface of the metal.

Results—The specimens were cleaned and examined in the usual way. Only slight honeycomb pitting, too shallow to be measured with a spherometer, was found on the surface. Areas that had been protected by the white deposit stood out in relief from the general surface by distances not exceeding 10 mils. The losses in weight of the specimens after derusting are given in Table IV.

The main conclusions to be drawn from the results are :

(i) The conditions of exposure are reasonably uniform over the landing stage, the maximum deviation of the average loss in weight of the eight specimens on any one frame from the corresponding average for all frames being about 4%.

(ii) The rate of rusting of ordinary steel when immersed in sea water at Gosport for 1·2 yr. is 4·9 mils/yr. There is no information on the relation between the rate of rusting and the duration of exposure.

(iii) There is no difference, within the experimental error, between the rates of rusting in sea water of ordinary steel, copper-bearing steel, and ingot iron.

* The reference letters are those given to these materials in the Five Reports of the Corrosion Committee.

† The author is indebted to Mr. T. Henry Turner for this analysis.

(iv) The rate of rusting is about 15% less for Scottish wrought iron than for mild steel. When, however, this result is examined statistically, it is found that the probability that it is not mere chance is only slightly better than 0·5. For practical purposes, therefore, it must be concluded that the experimental data fail to reveal any certain differences between the resistance to corrosion by sea water of the four materials tested.

(v) There is some indication that a natural protective deposit may form locally on ferrous materials immersed in sea water.

Tests at Plymouth

Experimental Details—The tests carried out at Plymouth in 1940 were made on three groups of steels as follows :

(*a*) *O.T.U.A. Steels**—Specimens of nearly all the steels prepared for the corrosion tests organized in France by the Office Technique pour l'Utilisation de l'Acier (O.T.U.A.).[1, 2] The steels concerned were classed in four groups, namely :

* Available through the courtesy of the late Monsieur L. Seguenot.

Table V

ANALYSES OF THE STEELS TESTED AT PLYMOUTH

Steel	Code	Thickness, in.	Analysis, %*								
			C	Al	Cr	Cu	Mn	Mo	P	S	Si
(*a*) O.T.U.A. Steels (8 in. × 8 in.)											
(1) Low carbon steels											
(i) Basic Bessemer											
Rimming, ordinary†	*A1*	¼	0·05	...	...	0·04	0·64	...	0·06	0·02	0·20
,, high P	*A2*	¼	0·03	...	...	0·04	0·31	...	0·14	0·04	...
,, high P and S	*A3*	¼	0·03	...	...	0·05	0·30	...	0·10	0·07	...
(ii) Open-hearth											
Rimming, ordinary	*A4*	¼	0·13	...	...	0·09	0·33	...	0·03	0·03	...
,, from haematite pig	*A5*	¼	0·06	...	...	0·09	0·32	...	0·01	0·03	...
Killed, ordinary	*A6*	¼	0·10	0·04	...	0·04	0·35	...	0·03	0·02	0·10
,, from haematite pig	*A7*	¼	0·11	0·04	...	0·11	0·34	...	0·01	0·03	0·13
(2) Copper-bearing steels											
(i) Basic Bessemer											
Rimming, ordinary	*B1*	¼	0·05	...	...	0·53	0·43	...	0·05	0·05	...
,, high P	*B2*	¼	0·04	...	...	0·51	0·34	...	0·15	0·04	...
,, high P and S	*B22*	¼	0·06	...	...	0·48	0·53	...	0·14	0·07	...
(ii) Open-hearth											
Rimming, ordinary	*B3*	¼	0·11	...	...	0·50	0·42	...	0·03	0·03	...
Killed, from haematite pig	*B4*	¼	0·10	0·01	...	0·48	0·39	...	0·02	0·03	0·04
Dead soft, Mo 0·08%	*B6*	¼	0·03	0·01	...	0·48	0·26	0·08	0·02	0·02	...
(3) Mild steels											
Open-hearth											
Killed, ordinary	*C1*	¼	0·22	0·04	...	0·05	0·71	...	0·03	0·03	0·12
,, from haematite pig	*C2*	¼	0·21	0·03	...	0·03	0·58	...	0·02	0·03	0·03
(4) Chromium–copper steels											
(i) Basic Bessemer											
Killed, ordinary	*D1*	½	0·17	...	0·44	0·56	0·89	...	0·06	0·03	0·16
,, high P	*D2*	¼	0·10	...	0·42	0·65	0·99	...	0·11	0·06	0·18
(ii) Open-hearth											
Killed from haematite pig	*D4*	¼	0·22	0·01	0·51	0·41	0·91	...	0·03	0·03	0·23
,, high P	*D5*	¼	0·21	0·01	0·45	0·41	0·77	...	0·11	0·03	0·24
,, ordinary	*D6*	¼	0·12	0·01	0·49	0·43	0·79	...	0·03	0·03	0·22
(*b*) Aluminium–chromium Steels (6 in. × 4 in.)	*A9*	⅛	0·10	0·20	2·10	...	0·40	...	0·02	0·02	0·38
	A15	⅛	0·37	1·23	3·72	...	0·31	...	0·03	0·02	0·28
	APS10	⅛	0·11	1·30	2·30	0·09	0·58	...	0·02	0·02	0·40
(*c*) Other Steels (6 in. × 4 in.)											
Copper-bearing steel	*D*	5/16	0·02	...	...	0·06	0·03	...	0·01	0·04	...
Copper–manganese steel	*L*	¼	0·16	...	...	...	0·51	...	0·03	0·03	0·01
Mild steel, ship-plate quality	*M*	¼	0·22	...	...	...	1·47	...	0·05	0·05	0·14
Chromium–copper steel	*O*	½	0·14	...	...	0·32	0·58	...	0·03	0·04	0·02
Cr–Cu–P–Si steel	*R*	⅛	0·23	...	...	0·50	1·58	...	0·04	0·04	...
'D' steel	*T*	5/16	0·09	...	0·86	0·32	0·28	...	0·12	0·05	0·55
Ingot iron‡	*W*	⅛	0·27	...	0·61	0·48	0·90	...	0·04	0·03	0·15

* Three dots denote that the content of the element concerned is low
† The silicon content of 0·20% given by O.T.U.A. seems high for a rimming steel
‡ The analysis given is typical and not of the actual specimens

(1) Ordinary low-carbon steels with a tensile strength of about 25 tons/sq. in.
(2) Copper-bearing steels with a tensile strength of about 25 tons/sq. in.
(3) Ordinary mild steels with a tensile strength of about 32 tons/sq. in.
(4) Chromium–copper steels with a tensile strength of about 32 tons/sq. in.

(*b*) *Aluminium–chromium steels**—Portevin and Herzog had reported that steels containing low percentages of aluminium and chromium show good resistance to corrosion by sea water.[3, 4] Specimens of three of these steels prepared from actual 15-ton heats made in a basic open-hearth furnace, were therefore included in the test.

(*c*) *Other steels*—Specimens of a chromium–copper–phosphorus–silicon steel of American origin and of six irons or steels made in Great Britain were also included.

Analyses of the materials tested are given in Table V. The specimens varied in size, those of the O.T.U.A. steels being 8 in. × 8 in. × $\frac{1}{8}$ in. and the remainder 6 in. × 4 in. but of different thicknesses up to $\frac{1}{2}$ in. The area exposed to corrosion was 855 sq. cm. for the O.T.U.A. steels, 300 sq. cm. for the aluminium–chromium steels, and 342 sq. cm. for the other steels. The millscale was removed from all specimens before exposure by pickling in warm dilute sulphuric acid containing an inhibitor.

The specimens were immersed in the sea at Plymouth, for 203 days, from March to October 1940. They were attached to frames carried below a raft moored just inside the breakwater in Plymouth Sound. Each frame carried two rows of specimens immersed at depths of 20 in. and 36 in., respectively, measured to the top edge. Duplicate specimens were exposed throughout, the two specimens of each material being placed at different levels and generally on different frames.

Results—There was a heavy marine growth on all the specimens when they were removed from the water. The organisms present included grass, mussels, barnacles, anemones, and calcareous worms. There was no significant difference in the fouling of individual specimens.

Gross fouling was removed at the raft and the specimens were returned to the laboratory where the rust was removed by wire-brushing followed by immersion in warm dilute sulphuric acid containing an inhibitor. The acid treatment cleaned the surface easily and the hydrogen evolution was negligible. After a final weighing, the surface of the specimens was examined.

No pitting of any consequence that could be attributed to corrosion by sea water was found on any of the steels except the three aluminium–chromium steels. These had suffered appreciable local attack, especially round the suspension holes. Pits up to 26 mils deep were observed on the specimens of steel *A*9 and one of them had been perforated by corrosion at a stamped identification mark. Steel *APS*10 had also pitted to a depth of 20 mils.

The results of the loss in weight test are given in Table VI. To eliminate the differences in the surface area exposed the losses in weight have been converted into the equivalent corrosion rates in mils/yr.

Conclusions—The average experimental error for the whole series, expressed as half the percentage difference between duplicates, was 3·1%, *i.e.*, $100(a-m)/m$, where a is the loss in weight of the more corroded specimen and m the mean loss in weight of the pair. Differences between materials of less than about 10% are insignificant. Moreover, owing to the differences in the sizes of the specimens, the results for the O.T.U.A. steels of group (*a*) are not strictly comparable with those of the steels in groups (*b*) and (*c*).

O.T.U.A. Steels—There is no marked variation in the corrosion resistance, under the conditions of the experiment, of the commercial structural steels tested by the French Corrosion Committee. The overall variation in the figure for the corrosion rate is from

Table VI

CORROSION RATES OF STEELS (PLYMOUTH TESTS)

Steel	Code	Corrosion Rate, mils/yr.		
		Individual Steels	Averages	
(*a*) O.T.U.A. Steels				
(1) Low carbon steels				
Basic Bessemer	*A*1	5·7		
	*A*2	5·7		
	*A*3	5·9	5·8	
Open-hearth	*A*4	5·7		
	*A*5	5·6		
	*A*6	5·6		
	*A*7	5·4	5·6	5·66
(2) Copper-bearing steels				
Basic Bessemer	*B*1	6·0		
	*B*2	5·2		
	*B*22	5·1	5·4	
Open-hearth	*B*3	6·1		
	*B*4	5·8		
	*B*6	5·7	5·9	5·65
(3) Mild steels				
Open-hearth	*C*1	5·7		
	*C*2	6·3	6·0	6·0
(4) Chromium–copper steels				
Basic Bessemer	*D*1	6·2		
	*D*2	5·5	5·8	
Open-hearth	*D*4	6·5		
	*D*5	5·8		
	*D*6	6·4	6·2	6·08
(*b*) Aluminium–Chromium Steels				
Al 0·2%, Cr 2·1%	*A*9	4·7		
Al 1·3%, Cr 2·3%	*APS*10	5·0		
Al 1·2%, Cr 3·7%	*A*15	5·3		5·0
(*c*) Other Steels				
Copper-bearing	*D*	6·8		
Copper–manganese	*L*	7·2		
Mild steel	*M*	7·9		
Chromium–copper	*O*	8·0		
Cr–Cu–Si–P	*R*	6·6		
'D' steel	*T*	8·7		
Ingot iron	*W*	7·8		

* Kindly supplied by Dr. E. Herzog.

5·1 mils/yr. for steel *B*22 to 6·5 mils/yr. for steel *D*4. The individual weight losses for the specimens show that the significance of the difference between them corresponds to a probability of 0·07, *i.e.*, according to statistical theory, the odds are 14 to 1 against this difference being due to mere chance. These are slightly shorter odds than the usual minimum of 19 to 1 generally required by statisticians for a result to be accepted as significant. The result may be taken, however, as showing a small but genuine difference between these two steels because, in the French tests on the same set of steels, steel *B*22 consistently lost less weight than steel *D*4 in total immersion tests at Monaco.* It is certain, however, that the smaller differences that occur between other steels of the group have little if any significance. In the main this agrees with Chaudron,[2] who concludes that the addition of chromium and copper to steel fails to stop corrosion, and that the copper-bearing open-hearth steel with a high phosphorus content *B*5, and the copper-bearing basic Bessemer steel *B*2, with a high phosphorus content, are generally the most corrosion-resistant in sea water. Unfortunately, steel *B*5 was missing from the set of specimens sent to England. Its analysis was 0·11% of C, 0·53% of Cu, 0·16% of P. Steel *B*2 is, however, similar to steel *B*22 (*see* Table V) and its corrosion resistance in the Portsmouth tests proved to be of the same order.

Chaudron confirms that other variants, such as whether the steel is rimming or killed, are without appreciable effect on the rate of corrosion, and that there is little difference between the rates of corrosion under totally immersed conditions at Boulogne and those at Monaco.

Aluminium–Chromium Steels and Other Steels—The results for these two groups of steels may be considered together because they were of the same overall size (6 in. × 4 in.), although they differed in thickness. Since the rate of corrosion at cut edges is not necessarily the same as that on rolled surfaces, the differences in the thickness of the material may have had some effect.

The average value of the corrosion rate for the three aluminium–chromium steels is 5·0 mils/yr., whereas the rates for the other steels vary from 6·6 to 8·7 mils/yr. This significant difference confirms the conclusion drawn by Portevin and Herzog that these steels, as a class, have a superior resistance to general attack in sea water than the average run of commercial structural steels. Unfortunately they have a tendency to pit ; this is often the case for metals on the borderline of passivity. Marked pitting has been observed also on similar specimens of the three aluminium–chromium steels totally immersed in Workington Harbour for a year.[5] In this test ordinary mild steel corroded at the rate of 4·0 mils/yr. and the three aluminium–chromium steels *A*9, *APS*10, and *A*15, at rates of 3·5, 3·3, and 4·6 mils/yr. respectively.

With the remaining steels (group *c*), there is no significant difference in the corrosion rates of mild steel *M*, chromium–copper steel *O*, and ingot iron *W*. The copper-bearing steel *D*, the copper–manganese steel *L*, and the Cr–Cu–P–Si steel *R* show lower corrosion rates than that of the mild steel and the rate for the copper–manganese steel *L* is higher than that for the copper-bearing steel *D*. Moreover, the rate is higher for ' D ' steel *T* than for ordinary mild steel *M*. Statistical analysis shows, however, that these differences have little significance, the values of the *t* function being 2·03 for the difference between steels *D* and *M*, 1·32 (*L*/*M*), 2·82 (*R*/*M*), 1·77 (*T*/*M*), and 1·24 (*L*/*D*). The highest value of *t*, that of 2·82 for steels *R* and *M*, corresponds to a slightly worse chance than 1 in 10 that the result is not fortuitous. Hence, it would be unwise to regard these results as more than possible indications of behaviour, to be verified by further experimental work.

In the whole series of tests there was no marked difference in the corrosion rate with depth of immersion. In 16 cases out of 30 the specimen in the upper row, immersed at a depth of 20 in. had suffered a greater loss in weight than its duplicate in the bottom row at a depth of 36 in. This indicates virtual equality of the conditions of exposure in the two rows and confirms the conclusion drawn from the Gosport tests that the conditions of immersion become reasonably uniform at depths exceeding 14 in.

Tests at Emsworth (First Series)

Experimental Details—The results obtained for the group (*c*) steels exposed at Plymouth had given a slight indication of a difference in the respective

* Monaco is the only station for which detailed results are available (*see* Table XXXVII of ref. 2). The ranking values according to loss in weight of the two steels with reference to a set of 24 steels were as follows after increasing periods of immersion :

Steel *B*22	7th	5th	1st	3rd	7th
Steel *D*4	20th	13th	18th	18th	24th.

Table VII

ANALYSES OF IRONS AND STEELS TESTED AT EMSWORTH

Material	Analysis, %						
	C	Cr	Cu	Mn	P	S	Si
Staffordshire wrought iron *T*2	0·02	...	0·07	0·01	0·32	0·01	0·13
Ingot iron *W*	0·02	...	0·06	0·03	0·01	0·04	0·03
Mild steel *X*	0·20	...	0·02	0·59	0·04	0·04	0·02
' D ' steel	0·21	...	...	1·38	0·05	0·04	0·08
Cr–Cu–P–Si steel	0·09	0·84	0·33	0·26	0·11	0·05	0·55
Copper-bearing steel *Y*	0·21	...	0·22	0·59	0·04	0·03	0·03
Chromium–copper steel *L*	0·26	0·58	0·50	0·60	0·04	0·03	0·12
Copper–manganese steel	0·24	...	0·57	1·60	0·04	0·04	0·34

corrosion rates of chromium–copper steels and of mild steel when immersed in sea water, although there was no evidence of this in the parallel tests made on the French steels of group (*a*). A further test was carried out on larger specimens. Thirty-two specimens of the standard 15-in. × 10-in. × ⅜-in. size were used, representing Staffordshire wrought iron, ingot iron, and six steels. The analyses of the eight materials are shown in Table VII, two of them, ' D ' steel and Cr–Cu–P–Si steel, were supplied* from steelworks stock and were ½ in. thick instead of ⅜ in. A suitable correction has been applied for this difference in thickness.

The millscale was removed from all the specimens by pickling in cold 5% by volume hydrochloric acid before they were exposed. With the collaboration of Dr. I. G. Slater and Mr. L. Kenworthy, the test took place under conditions of complete immersion in sea water at the Admiralty Corrosion Committee's testing station at the Emsworth Swimming Pool from March 1944 to March 1948. It was originally intended to remove two of the four specimens of each material after two different periods of exposure. All the specimens, however, were removed after four years' immersion.

Results—All the specimens were heavily fouled and the final removal of the rust and fouling took a considerable time; the methods adopted have already been described (*see* p. 125).

The results, which relate to four specimens in each case, are shown in Table VIII. In addition to the average corrosion rate in mils/yr., figures are given for the average loss in weight and for the standard deviation of this average loss, so that the statistical significance of the results can be assessed. Values of the *t* function for the loss in weight of each material as compared with that of mild steel *X* have been calculated and the corresponding probabilities that these differences are due to mere chance are given in the last column.

The interpretation of the results is mainly a matter of statistics. There are strong indications that the observed behaviours of the Cr–Cu–P–Si steel, which had corroded less than mild steel *X*, and of ' D ' steel, which had corroded more than the mild steel are genuine. There is slight evidence that ingot iron *W* has resisted corrosion a little better than the mild steel, but this is at variance with the results of earlier experiments. Otherwise there is little to choose between all the materials.

Tests at Emsworth (Second Series)

Experimental Details—The materials used for the most recent, and from many points of view the most interesting of these series of tests, were derived from 59 laboratory heats of ordinary and low-alloy steels representing 57 different compositions,* which had been prepared on a collaborative basis in the laboratories of five members of the Corrosion Committee. The weight of ingot varied from 20 to 100 lb. and the size of ingot from 2¼ in. square to 4½ in. square. These ingots were rolled down in the laboratory of another member of the Committee and specimens for various tests were prepared. Four 3-in. × 2½-in. × ⅛-in. specimens of each steel were prepared for total immersion tests in sea water.

The steels used fall into six groups, namely :

(*a*) *Plain Carbon Steels* (12)—These comprised two sets of four steels with carbon contents of 0·1, 0·2, 0·4, and 0·6%, respectively, similar heats of which were made in different laboratories. A single 0·2% carbon steel with a high manganese content was also included. In addition the basis 0·1% carbon steel was repeated in the other three laboratories. Thus there were 12 steels in this group.

(*b*) *Cr–Cu–P–Si Steels* (19)—There were 17 steels containing small percentages of one or more of the elements chromium, copper, phosphorus, and silicon. Most of them contained 0·1% of carbon, and a few 0·2%. Two odd steels containing 0·5% of copper with 0·5 and 1·7% of manganese, respectively, were also classed in this group.

(*c*) *Al–Cr–Si Steels* (4)—There were four aluminium–chromium steels similar in composition to the steels tested in group (*b*) at Plymouth (*see* p. 128).

(*d*) *Cr–Cu–Ni Steels* (5)—This group consisted of

* Through the courtesy of the late Dr. T. Swinden.

* Duplicate heats of two compositions were made under the same conditions and both were tested.

Table VIII

CORROSION RATES OF SPECIMENS IMMERSED AT EMSWORTH FOR FOUR YEARS

Material	Average Corrosion Rate, mils/yr.	Loss in Weight, g./specimen		Statistical Test	
		Average	Standard Deviation	*t*	Probability*
Cr–Cu–P–Si steel	1·79	292	46	3·42	0·01
Ingot iron *W*	2·21	362	41	1·78	0·13
Chromium–copper steel *L*	2·35	384	25	1·21	0·28
Copper–manganese steel	2·35	385	62	0·88	0·42
Staffordshire wrought iron *T2*	2·41	395	35	0·80	0·46
Copper-bearing steel *Y*	2·49	408	22	0·45	...
Mild steel *X*	2·57	421	55	...	...
' D ' steel	3·27	537	42	3·65	0·01

* Probability that the difference between the loss in weight of the material concerned and that of mild steel *X* is due to chance, e.g., for the Cr–Cu–P–Si steel the odds are 99 to 1 against this, whereas for Staffordshire wrought iron *T* they are nearly equal, 46 for to 54 against

Table IX

REPRODUCIBILITY OF THE RESULTS FOR DIFFERENT CASTS OF 0·1% CARBON STEEL

Steel No.	Analysis, %					Corrosion Rate, mils/yr.
	C	Mn	P	S	Si	
1	0·11	0·65	0·03	0·05	0·18	2·77
6	0·10	0·48	0·06	0·05	0·21	2·80
27	0·15	0·69	0·05	0·05	0·27	2·68
36	0·10	0·34	0·02	0·01	0·17	2·82
47*	0·09	0·47	0·02	0·04	0·13	2·35
Average for first four steels						2·77

* This steel contains 0·22% of Cu

five steels containing up to 1% each of chromium or copper and up to 3% of nickel.

(*e*) *Cr–Mo–Ni Steels* (6)—These six steels contained 0·5% of molybdenum, together with additions of up to 3% of chromium and/or nickel. In one case 0·5% of copper was also present.

(*f*) *Other Steels* (11)—This group consisted of ten 0·1% carbon steels containing a few tenths of a per cent. of arsenic plus copper, beryllium, bismuth, lead, molybdenum, niobium, antimony, tin, tantalum, or tungsten. An eleventh steel intended to contain cadmium was found on analysis to contain only 0·01% of this element. Presumably the bulk of it had been lost by volatilization from the heat. Apart from the steel to which arsenic and copper were deliberately added, and one other steel made in a different laboratory, all these steels contained 0·2% of copper, which was inadvertently introduced in the scrap used for the charge.

The four specimens of each steel included two pairs, each of which had been heat-treated in a different way, as follows :

Treatment A : Heat to 900° C. ; soak for 30 min. ; cool in the furnace to 650° C. ; hold for 1 hr. ; cool in air.

Treatment B : Heat to 900° C. ; soak for 30 min. ; quench in lead at 450° C. ; soak for 5 min. ; cool in air.

The specimens were descaled before exposure by electrolytic pickling. They were immersed in the Admiralty Corrosion Committee's testing tank at Emsworth in August 1946 and a complete set of two specimens of each steel was removed two years later in August 1948, leaving two specimens of each steel. The two specimens removed included one that had been heat-treated by each of the different treatments given above. The results did not reveal any systematic effect of the method of heat-treatment upon corrosion resistance.

The removed specimens were found to have fouled heavily and after a rough cleaning at the exposure station, they were returned to the laboratory where coarse rust and remaining marine growths were removed by scraping and wire-brushing. The remainder of the rust was removed by treatment in cold dilute sulphuric acid containing an inhibitor, followed by washing and a final treatment with Clarke's solution. The specimens were weighed both after the rough mechanical cleaning and after the final treatment in the derusting baths. The correlation between the ranking orders of the losses in weight at these two stages is 0·54, which is reasonably good.

Results—The simplest method of presenting the results is to consider each of the major groups of steels individually, and to study the effect of variations in the alloying element within each group.

(*a*) *Plain Carbon Steels*—The reproducibility of the results for different casts of the basis 0·1% carbon steel, as made by different laboratories, is shown in Table IX. The agreement is fairly good, if steel No. 47 containing 0·2% of copper is omitted. Such differences as occur are well within the experimental error.

The effect of increasing carbon content is shown by the results given in Table X for the duplicate sets of four steels cast in different laboratories. The analyses given are mean values for both steels with the same nominal carbon content.

The differences between the first three pairs of steels are not significant but it is probable that the corrosion rate is significantly greater for the 0·6% carbon steels than for the others. If steels Nos. 4 and 39 are compared with steels Nos. 1 and 36, the probability that the difference between the average values for the two pairs is due to chance is 0·088 ; if the comparison is made between steels Nos. 4 and 39 and the other six steels of this sub-group, the probability is even less, namely 0·004 ; *i.e.*, it is a 250 to 1 chance against there being no real difference in the behaviours of the 0·6% carbon steels and the other steels with lower carbon contents.

The effect of a high manganese content is not clear, as will be seen from a study of the results for the two pairs of steels shown in Table XI. The two copper-bearing steels referred to in this Table should strictly be classed in group (*b*) but the results for them are most conveniently considered here. There is a possible indication that corrosion resistance decreases with

Table X

EFFECT OF CARBON CONTENT

Steel Nos.		Carbon, % (nominal)	Analysis, %			Corrosion Rate, mils/yr.		
I	II		C	Mn	Si	I	II	Mean
1	36	0·1	0·11	0·50	0·18	2·77	2·82	2·80
2	37	0·2	0·18	0·53	0·16	2·81	2·50	2·66
3	38	0·4	0·40	0·67	0·13	2·72	2·68	2·70
4	39	0·6	0·58	0·69	0·18	3·01	3·20	3·11

Table XI

EFFECT OF HIGH MANGANESE CONTENT

Manganese Content	Ordinary Steels (0·16% of C, 0·14% of Si, 0·01% of Cu)			Copper-bearing Steels (0·19% of C, 0·17% of Si, 0·52% of Cu)		
	Steel No.	Mn, %	Corrosion Rate, mils/yr.	Steel No.	Mn, %	Corrosion Rate, mils/yr.
Normal	2	0·62	2·81	8*	0·52	2·50
High	5	1·82	3·01	7	1·71	2·60

* Steels 2, 5, and 7 were made in the same laboratory but steel 8 in a different one

increasing manganese content, although statistically the differences are not significant. In the previous series of tests at Emsworth a 'D' steel with a high manganese content corroded more than an ordinary mild steel (*see* Table VIII).

(*b*) *Cr–Cu–P–Si Steels*—The results for the chromium–copper–phosphorus–silicon groups of steels are given in Tables XII and XIII which relate to steels containing 0·1 and 0·2% of carbon respectively.

The resistance to corrosion is shown to be materially increased by the addition of chromium. If variations in the other alloying elements are disregarded and averages taken for all the steels with the same chromium content, it will be found that there is a progressive and highly significant improvement in performance as the chromium content rises. The steels containing 2·5% of chromium are on the average more than twice as resistant as those to which no chromium has been added.

If the results are studied by arranging the steels in pairs of low and high copper, low and high phosphorus, or low and high silicon contents, none of these elements is shown to have any significant effect on corrosion resistance.

(*c*) *Al–Cr Steels*—The figures given in Table XIV for the aluminium–chromium steels show that these have proved much less corrodible than the basis ordinary 0·1% carbon steel. The figure of 0·97 mils/yr. recorded for the corrosion rate of steel No. 30, is the lowest for any of the 59 steels included in these tests. It is not clear, however, whether the aluminium content of the steel plays a major part in promoting corrosion resistance in steels containing both aluminium and chromium, because the differences between the figures of 1·08 and 1·19 mils/yr., for steels Nos. 28 and 29, which contain 2·6% of chromium and little aluminium, and that of 0·97 mils/yr. for steel No. 30, which contains 2·8% of chromium

Table XII

CORROSION OF Cr–Cu–P–Si STEELS WITH 0·1% OF CARBON

Steel No.	Approximate Analysis, %*				Corrosion Rate, mils/yr.	
	Cr	Cu	P	Si	Individual Steels	Average
6	Low	Low	Low	0·2	2·80	2·67
11		Low	Low	0·8	2·66	
12		Low	0·15	0·2	2·81	
18		0·5	Low	0·8	2·42	
13		0·5	0·15	0·2	2·67	
9	1	Low	Low	0·2	2·03	1·88
17		Low	Low	0·8	1·80	
14		Low	0·15	0·2	1·92	
15		0·5	Low	0·2	1·87	
20		0·5	0·15	0·8	1·78	
21	1·5	Low	Low	0·2	1·78	1·84
23		0·5	Low	0·2	1·90	
19	2	Low	Low	0·2	1·48	1·51
24		0·5	Low	0·2	1·53	
22	2·5	Low	Low	0·2	1·15	1·26
25		0·5	Low	0·2	1·36	

* 'Low' denotes that no deliberate addition of the element concerned was made to the charge and corresponds to a figure of the order of 0·01–0·05%

Table XIII

CORROSION OF Cr–Cu–Si–P STEELS WITH 0·2% CARBON

Steel No.	Approximate Analysis, %				Corrosion Rate, mils/yr.
	Cr	Cu	P	Si	
8	Low	0·5	Low	0·2	2·50
10	1	Low	Low	0·2	2·23
16	1	0·5	Low	0·2	1·99

and 1·4% of aluminium, are not significant. On the other hand, the difference between the rate of 1·57 mils/yr. for steel No. 26, containing 1·6% of aluminium alone, and that of 2·68 mils/yr. for the basis mild steel No. 27 is certainly significant, since analysis of the detailed results shows that the significance level is appreciably higher than 0·01, *i.e.*, the odds are more than 100 to 1 that the conclusion is well founded. The effects of aluminium and chromium are not additive, as shown by results given in Tables XII and XIII, for steels containing chromium alone. A corrosion rate of about 1·15 mils/yr. would be expected for a steel with 2·7% of chromium, which is not very much greater than the observed value of 0·97 mils/yr. for steel No. 30, which also contains 1·4% of aluminium.

(*d*) *Cr–Cu–Ni Steels*—The results for the group of steels containing percentages of chromium, copper, and nickel are shown in Table XV. The figures show that nickel additions have a perceptible effect in reducing the corrosion of steel; for example, the corrosion rates observed for steels Nos. 31 and 32 are significantly less than the rate for the unalloyed steel No. 27. Comparison of steels Nos. 31 and 33 with steels Nos. 32 and 34, respectively, renders it doubtful whether additions of copper exert any influence. In the main, however, chromium is the most potent element in increasing corrosion resistance. From the data given in Table XII steels containing 1% of chromium would be expected to corrode at the rate of about 1·92 mils/yr., as compared with 2·68 mils/yr. for the basis steel No. 27. The further improvement to an average value of 1·57 mils/yr. for steels Nos. 33 and 34 is to be ascribed to the presence in these steels of 3% of nickel.

(*e*) *Cr–Ni–Mo Steels*—The results for this group of steels are set out in Table XVI. Analysis of the loss in weight figures for the individual specimens shows that the significance level of the difference between

Table XIV

CORROSION OF Al–Cr STEELS

Steel No.	Approximate Analysis, %			Corrosion Rate, mils/yr.
	Al	Cr	Si	
27	Low	Low	0·3	2·68
28	Low	2·6	0·3	1·08
29	0·1	2·6	0·3	1·19
26	1·6	Low	0·2	1·57
30	1·4	2·8	0·8	0·97

Table XV

CORROSION OF Cr–Cu–Ni STEELS

Steel No.	Approximate Analysis, %			Corrosion Rate, mils/yr.
	Cr	Cu	Ni	
27	Low	Low	Low	2·68
31	Low	Low	3	2·15
32	Low	0·5	3	2·16
35	Low	1	1·5	2·24
33	1	Low	3	1·60
34	1	0·5	3	1·54

the rate of corrosion of the basis mild steel No. 36, 2·82 mils/yr., and that of the 0·5% molybdenum steel No. 40, 2·55 mils/yr., is 0·095. Thus it is about a 10 to 1 chance that the observed difference is genuine. This conclusion is supported by the lower rate observed for steel No. 41, 2·34 mils/yr. Steel No. 41, however, contains 0·2% of nickel and 0·5% of copper in addition to the 0·5% of molybdenum.

The effect of nickel in reducing the corrosion rate is brought out by the result for steel No. 43, containing 2% of nickel and 0·5% of molybdenum, which has proved about 25% more resistant than the basis steel No. 36.

The value of chromium additions is again marked. Steel No. 46, containing 3% of this element together with 0·5% of molybdenum and 0·1% of nickel, has given the low corrosion rate of 1·09 mils/yr. This figure is in good agreement with the values recorded for steels Nos. 22 and 25 (*see* Table XII), 28 and 29 (*see* Table XIV) all of which contain about 2·5% of chromium; these values are 1·15, 1·36, 1·08, and 1·19 mils/yr., respectively.

(*f*) *Other Steels*—The results observed for the miscellaneous group of steels, in which straightforward alloying additions of fractional percentages of various elements were made, are presented in Table XVII. All these steels except two, contained 0·2% of copper in addition to the desired alloying elements. It is not clear how far this common factor can be disregarded, although the bulk of the evidence so far presented shows that the presence of this small percentage of copper would not materially affect the rate of corrosion of the steels when immersed in sea water.

Table XVI

CORROSION OF Cr–Mo–Ni STEELS

Steel No.	Approximate Analysis, %			Corrosion Rate, mils/yr.
	Cr	Mo	Ni	
36	Low	Low	Low	2·82
40	Low	0·5	Low	2·55
41*	Low	0·5	0·2	2·34
43	Low	0·5	2	2·13
42	1	0·5	Low	1·65
44	1	0·5	3	1·50
46†	3	0·5	0·1	1·09

* This steel contains 0·5% of Cu

† The carbon content of this steel is nearly 0·2% but it is improbable that this affected the result

Table XVII

EFFECTS OF SUNDRY LOW-ALLOY ADDITIONS ON THE RATE OF CORROSION OF MILD STEEL

Steel No.	Alloying Elements	%	Corrosion Rate, mils/yr.
47*	None	...	2·35
48	Antimony	0·3	2·43
49	Arsenic and Copper	0·5 / 0·7	2·28
60	Beryllium	0·3	1·77
53	Bismuth	0·2	2·64
51	Cadmium	0·01†	2·56
52	Lead	0·2	2·40
58‡	Niobium	0·3	2·40
59‡			2·28
57	Tantalum	0·6	2·26
50	Tin	0·6	2·42
45	Vanadium	0·2	2·53
54‡	Tungsten	0·5	2·35
55‡			2·25

* This steel and all the other steels of this group with the exception of Nos. 49 and 45, the latter of which was made in another laboratory, contained about 0·2% of copper
† A content of 0·5% was intended but the cadmium was probably lost by volatilization in the furnace
‡ Duplicate heats

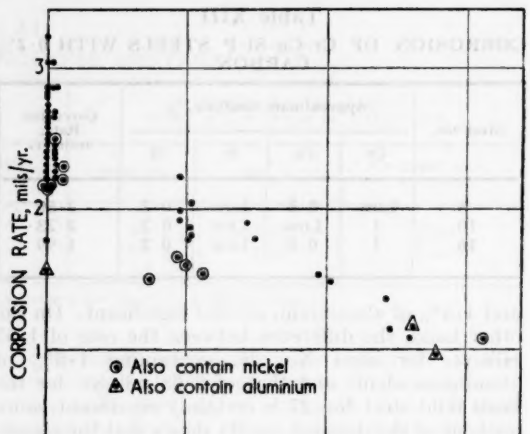


Fig. 2—Effect of chromium content on the rate of corrosion of steels totally immersed in sea water at Emsworth

None of the alloying elements concerned has had any significant effect on the corrosion rate, with the possible exception of beryllium (steel No. 60). It would be unwise, however, to attach too much importance to the results of this individual test, particularly as the significance level of the difference between the rate of corrosion of this steel and that of the basis steel No. 47 proves to be low. The value of the *t* function for this difference is 2·3, which, for two pairs of duplicates, corresponds to a probability of the order of 0·2 ; *i.e.*, the significance of the result is low, and the chance that it is correct may be little better than 5 to 1. Further tests on a larger scale are, therefore, desirable to verify or disprove this conclusion.

Pitting—The discussion of the results has been based solely on rates observed for general rusting and no reference has been made to any effects of pitting. Some roughening of the surface and localized attack at the edges and corners was observed for individual specimens in 35 cases out of a total of 117 specimens.* The pits were distributed more or less evenly between the various groups of steels, *i.e.*, there is no evidence of a connection between local attack and steel composition. With one exception, no pit of measurable depth was noted and, as it is particularly difficult to assess pitting on such small specimens, no attempt has been made to take this factor into account.

Cast Irons—Specimens of four cast irons were exposed to test alongside the steels. They were prepared by the British Cast Iron Research Association with the collaboration of Mr. W. Westwood. The compositions of the cast irons and their rates of corrosion are given in Table XVIII. In certain respects, notably in its tendency to suffer graphitic corrosion, cast iron differs from steel, and more

* In the case of one steel one specimen only was available for exposure.

Table XVIII

CORROSION OF VARIOUS CAST IRONS

Cast Iron		Analysis, %*					
No.	Type	Carbon		Mn	P	Si	Corrosion Rate, mils/yr.
		Total	Graphitic				
61	High-phosphorus iron	2·98	1·91	0·49	1·18	1·50	2·12
62	General engineering iron	3·01	2·95	0·61	0·75	3·40	2·62
63	Low-alloy iron with 0·8% of Cu†	2·90	2·78	0·54	0·59	2·97	2·67
64	Malleable iron‡	3·08	...§	0·28	0·05	0·50	3·17

* In all cases the sulphur content was 0·02–0·03%
† This iron contains 0·76% of copper
‡ The analysis refers to the material before annealing
§ The percentage of graphitic carbon in the annealed casting will vary with the distance from the surface

experience of testing this material is desirable, but these results suggest that the rate of general corrosion of cast iron when immersed in sea water may be considerably affected by its composition and somewhat less for certain types of cast iron, than for ordinary mild steel.

CONCLUSIONS

The following conclusions may be drawn from the tests reported in this paper :

(1) Minor variations in composition and structure, such as may result from different manufacturing processes, have no significant effect on the rate of corrosion of ordinary mild steels when immersed in sea water.

(2) Of the wide range of elements added to the low-alloy steels tested, it can be said that only two, chromium and nickel, have an appreciable effect in reducing corrosion. The effect of chromium, which has the greater influence, is shown in Fig. 2. The rate of corrosion of all the steels immersed at Emsworth (Second Series) is plotted against chromium content. All variables in composition other than the chromium content are disregarded except that, in order to show the value of nickel additions to the steel and the possible effects of aluminium additions, the points for steels in which an appreciable amount of nickel or aluminium is also present have been distinguished from the others.

(3) There are indications—the conclusions can be put no more strongly than this—that the corrosion of ordinary steels by sea water increases when their carbon content rises above about 0·4% and is greater for steels with high manganese contents. Some increase in corrosion resistance towards sea water may result from the introduction of small percentages of aluminium or beryllium into the steel.

(4) There is no conclusive evidence that the presence of copper alone in the steel has any beneficial effect, although it is possible that this element may be of value when an increased percentage of phosphorus is also present.

Comparison with Other Work

These conclusions may be compared with those drawn from the results of other British researches in this field. The main authority, Dr. J. Newton Friend, was responsible for the corrosion tests on ferrous metals carried out by a Committee of the Institution of Civil Engineers over periods of 5, 10, and 15 years at Auckland (New Zealand), Colombo (Ceylon), Halifax (Canada), and Plymouth (England).[6] Unfortunately, the majority of the bars exposed in these tests, which were initiated over 30 years ago, were immersed without removal of millscale. This led to considerable pitting and may have influenced some of the results. However, in the main the results support the present conclusions. Friend concluded that under conditions of complete immersion in sea water the sulphur and phosphorus contents of the steel had little influence on the corrosion rate and that a steel with a carbon content of 0·35% was generally more corroded than one containing 0·24% of carbon. In the latter case the difference was not great and, taking an average value for the four testing stations, based on the weight losses, it was of the order of 12%.

The only low-alloy steels exposed in the tests of the Institution of Civil Engineers comparable with those included in the Corrosion Committee's tests are two steels containing 0·6% of copper and 3·8% of nickel, respectively; these were immersed in the as-rolled condition. Overall comparisons with a 0·24% carbon steel also exposed with the millscale show a slight superiority for the copper-bearing steel, about 13% when calculated as indicated above, and a more marked superiority, 22%, for the steel with 3·8% of nickel.

Friend also reports on the corrosion of descaled bars of 0·2% carbon steel. The rates of corrosion of this steel at Plymouth were 5·0, 3·3, and 2·6 mils/yr., over 5, 10, and 15 years, respectively. These figures agree reasonably well with those given in Table II for the results of the Corrosion Committee's tests in British waters.

Valuable confirmation of the effect of chromium in reducing the corrosion rate of steel immersed in sea water is given in a report on tests carried out in the Research Department of Messrs. Hadfields Ltd.* The tests were made on single round bars of eight different steels, 12 in. long by 1¼ in. dia. and with a machined

* The report was made available to the Marine Corrosion Sub-Committee through the courtesy of Mr. W. J. Dawson and Dr. S. A. Main.

Table XIX

RESULTS OF TOTAL IMMERSION TESTS* IN SEA WATER AT FREETOWN, SIERRA LEONE

Steel	Approximate Analysis, %						Corrosion Rate, Mils/Yr.
	C	Cr	Ni	Mn	Si	Other Elements	
Mild	0·24	0·11	0·23	0·80	0·25	...	15·2
Copper-bearing	0·13	...	...	0·48	0·03	Cu 0·28	17·0
3% Chromium	0·04	2·62	...	0·49	0·36	...	9·9
13% Chromium (rustless iron)	0·11	13·4	0·20	0·29	0·17	...	12·1
18/2 Cr–Ni	0·15	18·2	1·93	0·48	0·23	...	8·6
18/8 Cr–Ni	0·18	18·3	7·7	0·39	0·12	...	5·1
10/2/20/2 Cr–Cu–Ni–W	0·14	10·3	20·7	0·50	0·51	Cu 2·06, W 2·06	9·9
36% Nickel	0·08	...	36·4	1·25	0·14	...	6·9

* Carried out by the Research Department of Messrs. Hadfields Ltd.

surface. The bars were set with their ends in a heavy wooden frame and were then completely immersed in sea water at the end of the jetty at Whiteman's Bay, Freetown, Sierra Leone, for a total period of 220 days. An intermediate inspection, at which the specimens were cleaned and visually inspected, was made after 87 days.[7]

The results of this test are summarized in Table XIX, where the loss-in-weight figures determined by Messrs. Hadfields Ltd. have been converted into the equivalent rates of general corrosion in mils/yr. In the present connection the results for the copper-bearing steel and for the steel containing 3% of chromium are of chief interest. It will be seen that the copper-bearing steel shows a higher rate of corrosion than the ordinary mild steel, although it is doubtful whether this difference is significant as only single bars were exposed, and that the 3% chromium steel has corroded less. In fact, in their report the Research Department of Messrs. Hadfields Ltd. conclude that the practical use of this low-chromium steel under the conditions of the test would prove of economic advantage. They state that it was selected for trial on the basis of successful experience gained in its use as a component for sluice gates on the Nile and that subsequently it also behaved well in the form of bolts and nuts in practical trials in a pier in estuarine waters in East Africa. Since similar results are said to have been obtained in the United States, it may be regarded as established that low-chromium steels are particularly suitable for resisting corrosion when totally immersed in sea water. Portevin and Herzog[4] have also pointed out the value of chromium additions to steel intended to resist sea-water corrosion. On the basis of the Corrosion Committee's results it seems reasonable to expect steels of this type to be at least twice as resistant as ordinary mild steel.

The figures given in Table XIX show that the rate of corrosion at Freetown was considerably higher than that observed in British waters (Table II). The result may be due in part to the higher temperature of the water, although the figure observed at Freetown would probably have been lower had the Committee's method of exposure been used, because in the Freetown tests heavy corrosion sometimes occurred at the ends of the bars embedded in the timber of the exposure frame. Moreover, the fact that the Freetown specimens were freed from fouling organisms for inspection after 87 days may have increased the average corrosion rate over the whole exposure period of 220 days.

Future Work

To confirm the effects of alloying steel with chromium and/or nickel (*see* p. 130), tests on large specimens rolled from full-scale commercial heats are needed. It would be at least of scientific interest to investigate further the effects of high carbon content, high manganese content, and of beryllium additions by tests of the same type. Studies of the corrosion resistance of steels should also be made under conditions in which they are moving through the sea water ; it is possible that tests made on comparatively small specimens by means of a rotor apparatus designed in the B.I.S.R.A. Corrosion Laboratory might be useful in this connection.

Acknowledgments

In addition to the acknowledgments made in the text for the supply of materials and the provision of facilities, the author wishes to thank his past and present colleagues at the B.I.S.R.A. Corrosion Laboratory who have helped with the preparation, exposure, and inspection of the specimens, Dr. T. A. Banfield in the early stages, and more recently, Mr. G. P. Acock. The author also wishes to thank the numerous firms within the British iron and steel industry who prepared and presented the irons and steels of known composition exposed in the tests.

References

1. L. Seguenot : *Chimie et Industrie*, 1939, vol. 41, p. 87.
2. H. Baudot and G. Chaudron : *Revue de Métallurgie*, 1946, vol. 43, pp. 3–67.
3. E. Herzog : Private communication.
4. A. Portevin and E. Herzog : *Comptes rendus*, 1936, vol. 203, p. 1514.
5. T. Swinden and W. W. Stevenson : Private communication.
6. J. Newton Friend : Eighteenth Report of Deterioration of Structures in Sea Water, 1940, The Institution of Civil Engineers.
7. S. A. Main and T. H. Arnold : *Journal of The Iron and Steel Institute*, vol. 165, pp. 268–278.

British Welding Research Association

The Fifth Annual General Meeting of the Association was held at the Research Station, Abington, near Cambridge, on Thursday, 13th July, 1950, when the report of the Council, statement of accounts, and balance sheet were received and adopted. Dr. J. H. Paterson, introducing the report, expressed the Council's satisfaction with the progress of researches ; the new work undertaken by the Research Board during the year had already proved its value and as the laboratory facilities and equipment increased, so the Association's contribution to the welfare of the Welding Industry and to the nation's industries as a whole would be a very substantial one.

The Liaison Department had been reorganized and placed on a firm footing ; the belief of the Council that it would usefully supplement the work of the Association by bringing the results of its work to bear directly on Members' problems had been fully justified.

The Council was anxious to obtain the most modern types of testing plant vital to its work and to this end a pulsating pressure testing plant, for fatigue testing pressure vessels, had been installed and a large tensile testing machine had been placed on order. These large and expensive equipments, however, demanded considerable laboratory space and the Council was therefore planning to build a fatigue-testing laboratory at Abington, thus releasing a portion of the old laboratories for much-needed expansion of other work. This new laboratory would cost about £20,000—a sum much beyond the amount which the Association could spare from its reserves, and an appeal for support would have to be made. The Chairman expressed the hope that Members would consider what they could do to help in the building of this laboratory and in increasing the Membership of the Association.

The Thermodynamic Background of Iron and Steelmaking Processes. II—Deoxidation

By F. D. Richardson

SYNOPSIS

The thermodynamic principles involved in deoxidation are discussed. A critical survey is made of the thermodynamic data available for solutions of oxygen and alloying elements in liquid iron, and the main deoxidation equilibria are summarized in two diagrams for 1600° C. and 1540° C. The general pattern of the results is discussed in terms of the interaction of dissolved oxygen and dissolved deoxidizer in the liquid metal.

AN understanding of the physical chemistry of the removal of oxygen from steel must rest on a knowledge of the chemistry of oxygen and of alloying elements in liquid and solid iron. This knowledge must be based not only on studies of these elements dissolved separately in iron, but also on studies of the manner in which the oxygen and the alloying elements influence the chemical behaviour of each other when in solution together. The nature of the deoxidation products and the type of solid or liquid solution which may be formed between them are also very important. The first part of this paper deals in a general way with the chemistry of deoxidation, whilst the second deals specifically with deoxidation by particular elements.

Since the thermodynamics of deoxidation is essentially the thermodynamics of solutions, it is expedient to employ activities. Activities in solution have already been discussed in a limited manner in Part I[31] and the same treatment is adequate for this paper. Except where otherwise indicated, the standard states (of unit activity) selected for the various substances participating in the deoxidation equilibria are the stable pure phases at the temperatures and pressures concerned. The symbols $a_{[X]}$ and $\gamma_{[X]}$ are used to represent the activity and activity coefficient of any dissolved substance X on this standard. It is, however, sometimes more convenient to choose the standard state so that the activity of any solute X is equal to its concentration at high dilutions. In such cases the activity coefficient is represented by the symbol $f_{[X]}$, this being equal to unity at very low concentrations. Such a standard is normally used for oxygen in liquid iron, and is so chosen that at the lowest concentrations, the activity is equal to the percentage by weight of oxygen in the metal.

Since solutions of oxygen in pure liquid iron obey Henry's law up to saturation (*see* Fig. 1), the activity on this standard is equal to the percentage concentration over the whole solubility range. The activity coefficient $f_{[O]}$ is correspondingly unity. The standard free energy change for the solution of oxygen,

$$\Delta G^\circ = -27{,}930 - 0{\cdot}57T,$$

as given by Dastur and Chipman[8] applies to the reaction

$$\tfrac{1}{2}O_{2(\text{gas at 1 atm.})} = [O] \text{ (at 1\% activity in liquid iron).}$$

PHYSICO-CHEMICAL BACKGROUND

Oxygen in Liquid Iron

The thermodynamics of oxygen in liquid iron have been carefully studied by Chipman[7, 8, 10, 27] and his co-workers. The limiting solubility, or the concentration at which free ferrous oxide separates from liquid iron, has been measured by Chipman and Fetters,[5] Taylor and Chipman,[37] and Körber and Oelsen.[23] The results show that at all concentrations the oxygen content of liquid iron in equilibrium with a suitable gas phase (such as a CO/CO_2 or an H_2/H_2O mixture) is proportional to the square root of the theoretical oxygen pressure. This indicates that the solution of oxygen may be represented by the equation

$$\tfrac{1}{2}O_{2(\text{gas})} = [O],$$

where [O] represents an oxygen *atom* in the liquid iron. It will be completely surrounded by six or so iron atoms as nearest neighbours, and will, of course, be quite different from a free gaseous oxygen atom. The results also show that up to the limiting concentration (0·22% by weight at 1600° C., according to Taylor and Chipman) the dissolved oxygen atoms have no significant influence on one another. The maximum solubility results of Körber and Oelsen are about 50% greater than those of Taylor and Chipman. The latter authors' results are accepted here as they are more consistent and agree well with the slightly earlier measurements of Chipman and Fetters.[5] The linear relation between the oxygen content of liquid iron and the ratio of water vapour to hydrogen pressure, which is proportional to the square root of the oxygen pressure, is shown in Fig. 1 for temperatures between 1695° and 1705° C. The variation of the limiting solubility with temperature in the presence of a separate phase of ferrous oxide is shown in Fig. 2.

Virtually nothing has been published on the thermodynamics of oxygen in solid iron in spite of its

Paper CP/10/3 of the Chemistry Department (based on paper SM/75/49 of the Steelmaking Division) of the British Iron and Steel Research Association, received 16th January, 1950.

Dr. Richardson is Head of the Nuffield Research Group in Extraction Metallurgy at the Royal School of Mines, London, and was formerly Superintending Chemist of the British Iron and Steel Research Association.

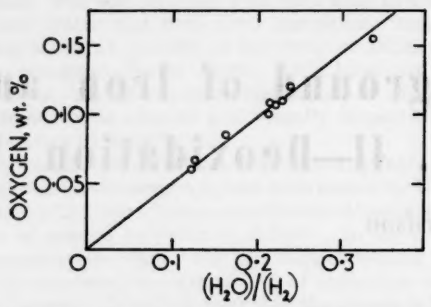


Fig. 1—Oxygen in metal as a function of steam/hydrogen ratio at 1695–1705° C. (Chipman and Samarin[7])

importance to an understanding of the deoxidizing reactions which occur as steel solidifies and cools further in the solid state. This represents a serious gap in present-day knowledge.

Alloying Elements in Iron

The behaviour of alloying elements in iron depends chiefly on how closely the element concerned resembles iron itself. For instance, Kubachewski and von Goldbeck[26] have shown that nickel behaves almost ideally in γ iron and the results of Jander and his co-workers[17, 18] suggest that liquid nickel, cobalt, and iron all behave ideally in binary mixtures of each other. The work of Körber and Oelsen[23] shows that liquid solutions of manganese and iron are ideal. On the other hand, aluminium,[4] silicon,[4] and carbon[27] are known to behave far from ideally. Relative to the pure liquid or solid elements and on an atom fraction basis, they have low activity coefficients in liquid iron. At 1600° C. for instance, at very low concentrations, $\gamma_{[Al]}$ and $\gamma_{[Si]}$ have values of 0·025 and 0·017 respectively, whilst $\gamma_{[C]}$ under similar conditions at 1540° C., is equal to 0·61.[4] The activity coefficients of other elements of interest here have not been established either in solid or liquid iron. For the present, therefore, it is suggested that ideality may reasonably be assumed in both solid and liquid solutions for alloying elements similar to iron (*e.g.*, chromium and possibly vanadium). This may not be done for alloying elements which are unlike iron or which form definite intermetallic compounds (*e.g.*, magnesium, boron, and titanium, the last of which is known to form the compounds Fe_2Ti, FeTi, and $FeTi_2$).

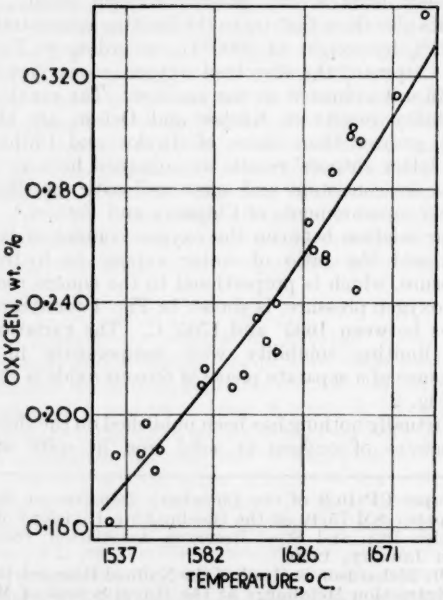


Fig. 2—Effect of temperature on the oxygen content of liquid iron (Taylor and Chipman[37])

Effect of Alloying Elements on the Activity Coefficient of Oxygen

Experiments have been made by Chipman and his co-workers[27, 2, 3] on the systems

$[C]$–$[O]$–$CO_{(gas)}$

$[Cr]$–$[O]$–$Cr_2O_{3\,(solid)}$ and $[Cr]$–$[O]$–$FeO.Cr_2O_{3\,(solid)}$

$[V]$–$[O]$–$V_2O_{3\,(solid)}$ and $[V]$–$[O]$–$FeO.V_2O_{3\,(solid)}$.

The results show that each of these alloying elements reduces the activity coefficient of the dissolved oxygen below the value in pure iron. The magnitude of the effect, represented in Fig. 3, increases markedly with the deoxidizing power of the alloying element and the stability of its appropriate oxide. This means that the deoxidizing elements do not function so successfully at high concentrations, as would be expected from their efficacy at low concentrations. The physical explanation of the effect must be some association between the atoms of oxygen and those of the alloying elements. This can best be pictured not in terms of precise compounds such as CrO and VO in the metal, but in terms of an uneven distribution or clustering of oxygen and deoxidizer atoms throughout the solution. Amongst the metallic atoms immediately surrounding the oxygen atoms, there is, on the average, a higher proportion of deoxidizer atoms than in the bulk of the solution.

In addition to the specific data already cited, there is evidence to suggest that silicon[42] and titanium[40] greatly lower the activity coefficient of dissolved oxygen. It is also to be expected that manganese should lower $\gamma_{[O]}$ by a factor of about 0·8 at 1% concentration by weight of manganese in iron, since its affinity for oxygen lies between that of chromium and that of vanadium.

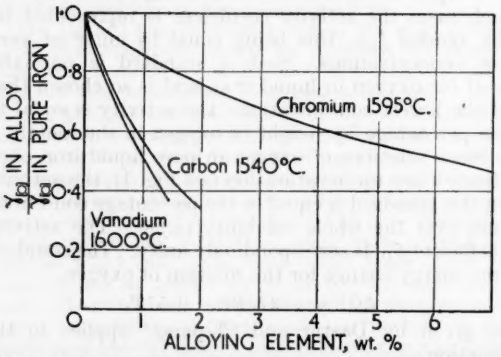


Fig. 3—Influence of alloying elements on the behaviour of oxygen in iron

Effect of Oxygen on the Activity of the Alloying Elements

Just as the activity coefficient of oxygen is reduced by the presence of the alloying elements, so the activity coefficients of these elements should themselves be lowered in the presence of dissolved oxygen. Since, however, under the conditions of interest in deoxidation equilibria, oxygen is normally present in far smaller quantities than the deoxidizing elements, this effect should be negligible.

Nature of the Deoxidation Products

In all deoxidation reactions each of the following equilibria can theoretically play a part :

$$[Fe] + [O] = (FeO)$$
$$\text{and } [X] + [O] = (XO),$$

where [X] is the deoxidizing element and (XO) the deoxidation product. Since free ferrous oxide cannot exist when the oxygen content of the iron falls below the saturation value, the first equilibrium cannot take part in deoxidation, unless ferrous oxide can occur at an activity less than unity in the deoxidation product. This is only possible if it can dissolve in the solid or liquid deoxidation product or can combine chemically with the oxide of the deoxidizing element.

An example of the first phenomenon is provided by deoxidation with manganese. The manganese oxide produced can dissolve iron oxide to give a liquid deoxidation product with a composition which is governed at any temperature by the equilibrium constant (K_T) for the reaction

$$[Fe] + (MnO) = (FeO) + [Mn],$$

so that

$$\frac{(FeO)}{(MnO)} = K_T \frac{[Fe]}{[Mn]}$$

Since liquid manganese and iron oxides behave ideally when mixed together, the composition of the oxide slag and hence the deoxidation product may easily be calculated, provided K_T and [Mn] are known. The relationship between (MnO)/(FeO) and [Mn] is shown in Fig. 4, which is based on the measurements by Chipman and co-workers[6, 12, 41] of slag metal equilibria involving manganese. The activity of (FeO) in the oxide slag is given by the equation

$$a_{(FeO)} = \frac{(FeO)}{(FeO) + (MnO)}$$

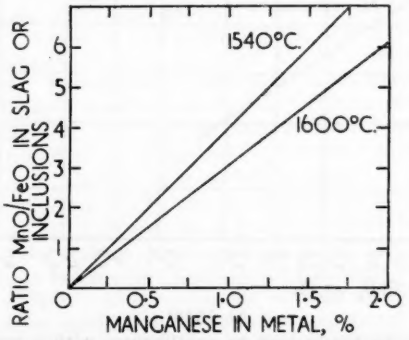


Fig. 4—Relation between composition of manganese-iron alloy and of the deoxidation product

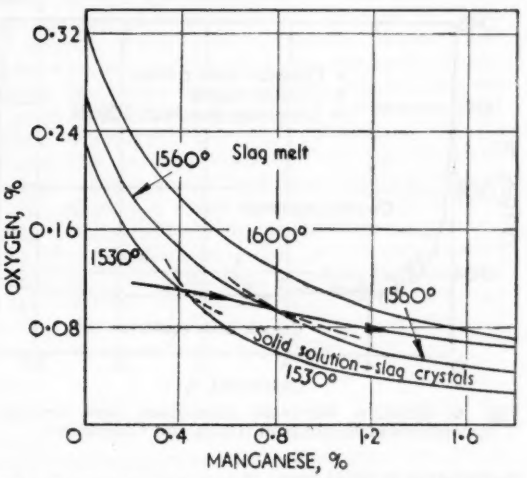


Fig. 5—Relation between manganese and oxygen contents of liquid iron, and solid and liquid deoxidation products (Körber and Oelsen[23])

From this it follows that

$$[O] = S \times a_{(FeO)},$$

where S is the solubility of oxygen in iron in equilibrium with pure ferrous oxide, as shown in Fig. 2. The effect of the inter-solubility of the ferrous and manganese oxides is to make the deoxidation more efficacious at low manganese contents than would have been the case if the formation of solid manganese oxide only had been possible.

It would be valuable to know more about the solid products of deoxidation which are obtained when the temperature of the steel falls below about 1550° C. Unfortunately, the phase diagram FeO–MnO is not sufficiently well established to ascertain whether these two oxides behave ideally in solid solution, although this is likely to be the case. Deoxidation when the product is solid should then be more efficient for the same residual manganese in the metal, since the manganese oxide in liquid slags at 1600° C. is well below the melting point of pure MnO. Figure 5, which is taken from Körber and Oelsen,[23] illustrates this point, although, as suggested above, the oxygen values are probably about 50% high.

An example of the effect of chemical combination between ferrous oxide and the oxide of the deoxidizing element is provided by chromium. At 1600° C. the stable solid spinel $FeO.Cr_2O_3$ (chromite) is formed at chromium concentrations below 6%, whereas solid Cr_2O_3 is formed at higher concentrations. The equilibria are expressed by the equations

$$[Fe] + 2[Cr] + 4[O] = FeO.Cr_2O_{3(solid)}$$
$$2[Cr] + 3[O] = Cr_2O_{3(solid)}$$

Typical results are shown in Fig. 6, taken from Chen and Chipman.[2] The effect of the formation of the spinel is to make deoxidation at low chromium contents more efficacious than it would have been had solid Cr_2O_3 been the only possible deoxidation product.

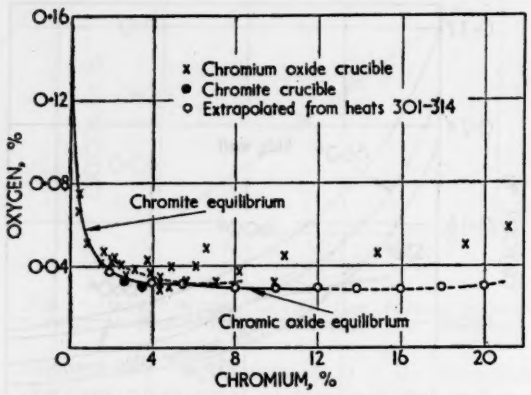


Fig. 6—Relation between chromium and oxygen contents of liquid iron (Chen and Chipman[2])

Deoxidation in Solid Iron

Little or no basic information is available on the interaction of oxygen and deoxidizing elements in solid iron. Except for carbon the activities of deoxidizing elements in solid iron are unknown, but it can reasonably be expected that elements like manganese and chromium will behave ideally. Elements with low activity coefficients caused by exothermic heats of solution in liquid iron, will have those coefficients lowered still further by cooling. The formation of the deoxidation products is, however, strongly exothermic and more so than the solution of the deoxidizing elements in solid iron, or than the formation of intermetallic compounds between the iron and the deoxidizers. It is therefore certain that deoxidation will continue in the solid state as the temperature falls. A further slow segregation of oxide products between the metal grains is thus thermodynamically possible and should occur by the slow diffusion of oxygen and deoxidizer in the solid metal. It is likely that this process becomes too slow to be observed below about 500° C.

DEOXIDATION BY SPECIFIC ELEMENTS IN LIQUID IRON

The deoxidation limits obtainable in liquid iron with the various elements in normal use are shown in Figs. 7*a* and *b* for the temperatures 1600° and 1540° C.; the estimated accuracies are indicated in the caption. The data on which the individual curves are based are discussed in detail later.

Aluminium

Aluminium is the most powerful deoxidizer in use and the normal product of deoxidation is solid alumina. Ferrous oxide is not soluble in solid alumina, and under equilibrium conditions the spinel $FeO.Al_2O_3$ can only be formed on solidification when

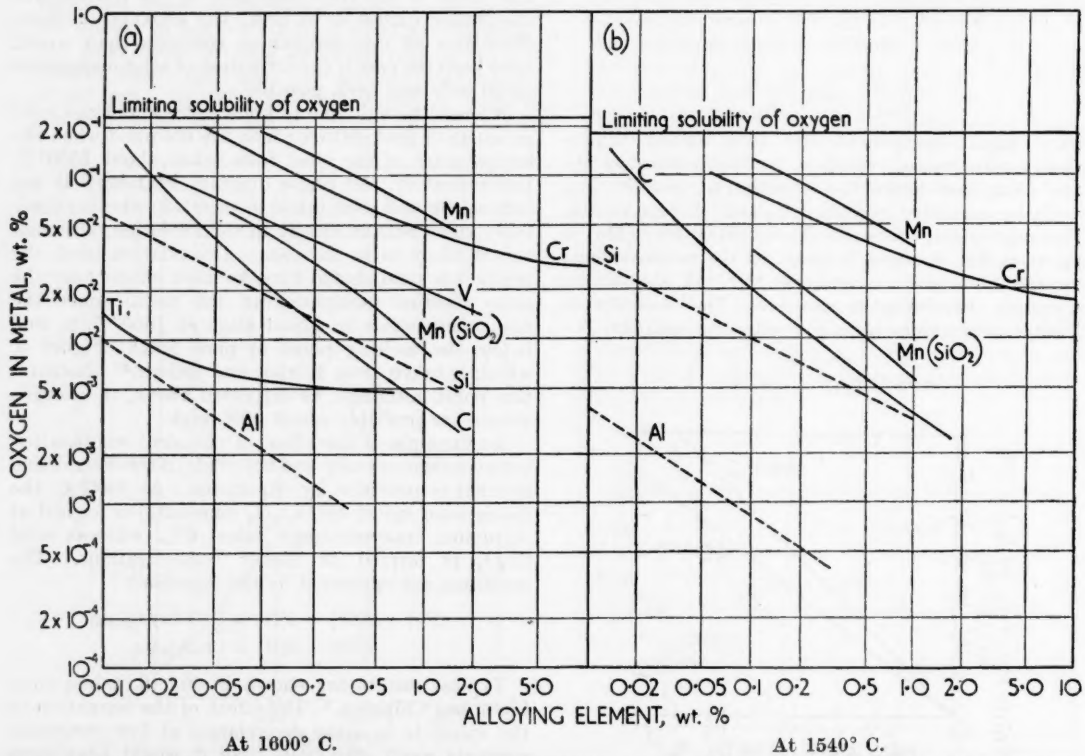


Fig. 7—Relation between percentages of oxygen and deoxidizer in liquid iron in equilibrium with a separate phase, (*a*) at 1600° C.; (*b*) at 1540° C. Full lines are probably correct to within a factor of 1·2; broken lines to within a factor of 2·0

the aluminium is present in the metal at very low concentrations. The relevant equilibrium equation is therefore,

$$2[Al] + 3[O] = Al_2O_{3(solid)}.$$

Wentrup and Hieber[39] obtained values of the equilibrium function $[Al]^2[O]^3$ expressed in terms of concentrations, by measuring the aluminium and oxygen contents of iron in alumina crucibles. Geller and Dicke[11] obtained values for the same constant in liquid iron by measuring the equilibrium between dissolved carbon (from 0·4 to 1·1%) and aluminium in alumina crucibles, and inferred the oxygen contents of the iron from the established data on the [C]–[O]–CO equilibrium. The equilibrium constant in terms of activities can also be obtained by calculation from the following thermal data :

$$2Al_{(liquid)} = 2[Al]_{(1\%\ concn.\ by\ wt.)}$$
$$\Delta G_{1808\text{–}1900^\circ K.} = -30{\cdot}08T$$
(Deduced from Chipman[4])

$$3/2O_{2(1\ atm.)} = 3[O]_{(1\%\ activity)}$$
$$\Delta G_{1808\text{–}2000^\circ K} = -83{,}790 - 1{\cdot}71T$$
(Deduced from Dastur and Chipman[8])

$$2Al_{(liquid)} + 3/2O_{2(1\ atm.)} = Al_2O_{3(solid)}$$
$$\Delta G_{930\text{–}2318^\circ K.} = -403{,}500 + 79{\cdot}2T.$$

The last equation is derived from the heat of formation of solid alumina by Snyder and Seltz[36] and from other thermal data recommended by Kelley.[22] The values of the constant (in terms of activities relative to the standard states indicated in the equations) derived in this way, are probably correct to within a factor of three. The experimental and calculated values are :

	1540° C.	1600° C.
Wentrup and Hieber's constants	6×10^{-12}	10^{-10}
Geller and Dicke's constants	4×10^{-14}	4×10^{-13}
Calculated constants	4×10^{-15}	7×10^{-14}

The large differences between these values may be accounted for in a number of ways. Wentrup and Hieber's oxygen concentrations may be too high, since complete separation of the alumina produced from the metal may not have been obtained. In addition the very small oxygen values are themselves subject to relatively large errors in analysis. Geller and Dicke's values may be too low on account of the influence of the carbon on the activity coefficient of the aluminium. It might at first be thought that carbon would lower the values of $\gamma_{[Al]}$ since aluminium is a fairly strong carbide former. Aluminium, however, interacts strongly with the iron as indicated by its low activity coefficient in iron alone. In both these respects it resembles silicon, whose activity coefficient in iron is increased by the presence of carbon.[4] Herasymenko[14] has pointed out that Geller and Dicke's results indicate that carbon increases $\gamma_{[Al]}$ strongly, and that this can be best appreciated from a plot of log K against [C] for the equilibrium,

$$3[C] + Al_2O_3 = 3CO + 2[Al],$$

where $K = [Al]^2/[C]^3$, expressed in terms of concentration. K decreases by a factor of about $10^{2.5}$ as the carbon content rises from 0·4 to 1·0%. A similar trend can be observed using Geller and Dicke's values for $[Al]^2[O]^3$, when similarly plotted against [C]. This effect would be quite sufficient to account for the difference between Geller and Dicke's, and Wentrup and Hieber's values for $[Al]^2[O]^3$; the increase in $\gamma_{[Al]}$ caused by the dissolved carbon would need to be approximately 5 times at 0·5% [O], and 15 times at 1·0% [C]. For the present, therefore, Wentrup and Hieber's values must be considered the most reliable. Because the values calculated from thermal data are so much smaller than those found by Wentrup and Hieber, it seems likely that aluminium greatly reduces the activity coefficient of the dissolved oxygen. If the whole of the difference were attributed to this effect, $\gamma_{[O]}$ would have to be lowered by a factor of approximately ten, at aluminium concentrations between 0·01% and 0·10%. This seems rather large at the lower aluminium concentrations and part of the difference may be attributed to errors in the thermal data used for the calculated constant or possibly in the values of $\gamma_{[Al]}$ in pure iron.

Boron

Deoxidation by boron has been investigated by Derge[9] and by Oelsen.[29] Both measured the equilibrium obtained in silica crucibles between [B] [Si] and [O] in liquid iron and B_2O_3–FeO–SiO_2 slags, while Derge also studied the deoxidation in magnesia crucibles.

The results are in poor agreement and are difficult to interpret, because nothing precise is known of the activities of B_2O_3 in such slags. It appears, however, that the deoxidation limits for boron in the presence of silica lie between those shown in Fig. 7 for manganese in the presence of silica, and those for carbon. A theoretical deoxidation constant for boron has been calculated by Gurry,[13] but this needs revision in the light of the more recent value for the heat of formation of boric oxide measured by Todd and Miller.[38] The constant which may be derived on the assumption that boron behaves ideally in liquid iron is

$$K_{1600^\circ C.} = \frac{a_{(B_2O_3)}}{[B]^2[O]^3} = 3 \times 10^{15},$$

where $a_{(B_2O_3)}$ is the activity of boric oxide in the slag relative to pure boric oxide and [B] is the percentage by weight of boron in the metal. The great difference between the very low deoxidation limits which may be calculated from this constant and the results of Derge and of Oelsen suggest that in liquid iron $\gamma_{[B]}$ is very low, and possibly less than 0·001. A lowering of $\gamma_{[O]}$ by the dissolved boron, similar to that experienced with aluminium may account for some of this difference, but hardly for the major part of it.

Carbon

The deoxidation by carbon has been thoroughly investigated by Marshall and Chipman[27] and their results have been used here.

Chromium

The deoxidation by chromium has been investigated fully by Chen and Chipman,[2] and their results, which are partly represented in Fig. 6, have been used.

Manganese

As explained previously the deoxidation product obtained when manganese is added to steel consists of a mixture of liquid manganous and ferrous oxides which behave ideally in solution together. The composition of the slags, in equilibrium with any

particular manganese content of the metal, can be calculated from the equilibrium constant for the reaction

$$[Mn] + (FeO) = (MnO) + [Fe].$$

It is a simple matter to calculate the oxygen content of the metal once the ratio of (FeO)/(MnO) has been calculated for the slag (*see* p. 139).

This equilibrium has been studied by a number of workers, the best known results being those of Körber and Oelsen.[23] The most precise data, however, are probably those available from slag–metal equilibrium studies of Chipman and others.[41] These results have recently been collated by Chipman, Gero, and Winkler[6] who propose the following equation :

$$\log\left(\frac{(MnO)}{(FeO)\,[Mn]_{(\%\text{ by wt.})}}\right) = 6440/T - 2\cdot82.$$

The effect of manganese on the activity coefficient of the dissolved oxygen has not been taken into account. 0·5% and 1% of Mn might lower $\gamma_{[O]}$ by the factors 0·9 and 0·8 respectively, compared with 0·52 for 1% [V] and 0·9 for 1% [Cr]. This effect is, however, within the error limits of the measurements.

Silicon

The reaction

$$[Si] + 2[O] = SiO_{2(solid)}$$

has been studied by Körber and Oelsen,[24] who measured the equilibrium between molten iron containing manganese and iron–manganese–silicate slags in silica crucibles. The slags were therefore saturated with silica, and the silica activity was that of solid silica at the temperature of measurement. They calculated values for the equilibrium constant, $K_T = [Si][O]^2$, from the functions [O]/(% FeO) and (% FeO)$^2 \times$ [Si] expressed in percentage concentrations by weight. K_T was calculated as $1\cdot34 \times 10^{-5}$ at 1550° C. and $3\cdot6 \times 10^{-5}$ at 1600° C. and agreed reasonably well with the few studies which they made in the absence of manganese.

Since it has already been suggested that Körber and Oelsen's values for the limiting solubility of oxygen in liquid iron are too high, it may be questioned whether it is justified to accept these values of K_T, which depend on their values for the constant [O]/(% FeO) in the presence of silica. At 1600° C. the activity of FeO in the system FeO–SiO_2 has been shown by Taylor and Chipman,[37] whose results have been discussed by Richardson,[30] to approximate to the molar fraction of ferrous oxide over the range, pure ferrous oxide to saturation with silica. As will be seen later in the discussion of the deoxidation by manganese in the presence of silica, this also holds for the system FeO–MnO–SiO_2 saturated with silica and for the temperature range 1540–1700° C. The [O]/(% FeO) values obtained by Körber and Oelsen *in the presence of silica* do, however, agree with those obtained by Taylor and Chipman for the system Fe–FeO when allowance is made for the conversion of molar fraction to percentage by weight.

Temp., °C.	[O]/(wt.-% FeO) (Körber and Oelsen)	[O]/(mol.-% FeO)	[O]/(activity FeO)
1550	0·0017	0·0019	0·185
1600	0·0021	0·0023	0·23
1650	0·0026	0·0029	0·28
1700	0·0030	0·0033	0·34

The values of K_T obtained by Körber and Oelsen may therefore be considered reasonably reliable.

Reference has already been made to the fact that silicon would be expected to reduce the activity coefficient of oxygen, and that the work of Zappfe and Sims[42] supports this view. The results of Körber and Oelsen would indicate that this effect is not very great up to 1% of silicon, which was the concentration range investigated by them. The scatter of their results, however, is such that $\gamma_{[O]}$ might well be reduced by the factor 0·5 at 1% of silicon, the effect being proportionately less at lower concentrations.

Titanium

This deoxidation has been studied by Wentrup and Hieber[40] who measured the oxygen and titanium contents of iron in equilibrium with the solid deoxidation product in alumina crucibles at 1600° C. At very low titanium contents 2FeO.TiO_2, FeO.TiO_2, and TiO_2 were obtained. With residual titanium contents greater than 0·2%, Ti_2O_3 was formed. Their results are shown in Fig. 8. As the titanium content of the metal was increased from 1 to 10%, the oxygen content of the metal increased from 0·004 to 0·010. This finding is in line with the known high solubility of oxygen in liquid titanium.

Deoxidation limits for titanium under conditions where TiO_2 is formed, may be calculated from the thermodynamics of the reaction

$$[Ti] + 2[O] = TiO_{2(solid)}.$$

The limits may be derived from the following equations :

$$Ti_{(solid)} + O_{2(1\text{ atm.})} = TiO_{2(solid)} \qquad \Delta G = -219{,}000 + 44\cdot26T$$

$$Ti_{(liquid)} = Ti_{(solid)} \qquad \Delta G = -4{,}190 + 2\cdot0T$$

$$[Ti]_{(1\%\text{ concn. by wt.})} = Ti_{(liquid)} \qquad \Delta G = +8\cdot8T$$

$$2[O]_{(1\%\text{ activity})} = O_{2(1\text{ atm.})} \qquad \Delta G = +55{,}860 + 1\cdot14T.$$

The first equation is based on the following data : $\Delta H_{25°\text{ C.}}$, of Roth and Wolf[32] ; the entropies at 25° C. of Ti[19] and O_2[21] by Kelley, and of TiO_2 by Shomate[34] ; the high temperature heat capacity data of Kelly[20] for Ti and O_2 and for TiO_2 by Naylor.[28] There is some doubt about the accuracy of $\Delta H_{25°\text{ C.}}$, which may be correct to only $\pm$ 5 kg.cal. The second equation is obtained by estimating the entropy of

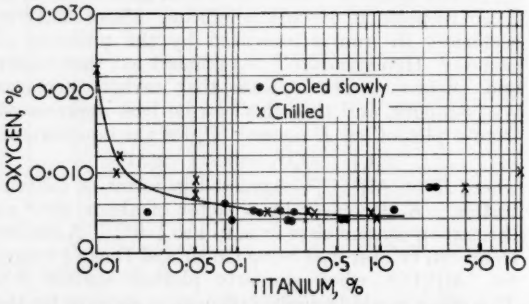


Fig. 8—Relation between solubility of oxygen in iron and the titanium content at 1600° C. (Wentrup and Hieber[40])

melting as 2 cal./degree ; the third equation assumes ideal behaviour for titanium dissolved in iron ; the fourth is based on Dastur and Chipman.[8] The value obtained for the constant $[Ti]\,[O]^2$ (expressed in terms of activities relative to the standard states indicated in the equation) is $10^{-7\cdot27}$ at 1600° C. This leads to deoxidation limits well below the values obtained by Wentrup and Hieber, and suggests low values for $\gamma_{[Ti]}$ and $\gamma_{[O]}$. The difference could be compatible with $\gamma_{[Ti]}$ of the order of 0·1, and a simultaneous lowering of the activity of the oxygen by a factor of 0·4 at 0·5% of titanium ; part of the difference may, however, be attributable to errors in the data used for the calculated constant.

Vanadium

The deoxidation equilibria in which vanadium is involved at 1600° C. have recently been studied by Dastur and Chipman,[3] who have shown that the appropriate equations are

$2[V] + 3[O] = V_2O_{3(solid)}$ (at vanadium concentrations greater than about 0·2%)

$2[V] + [Fe] + 4[O] = FeO.V_2O_{3(solid)}$ (at vanadium concentrations less than about 0·2%)

Samarin and Poliakov,[33] whose work has been reported in English by Case,[1] have studied the equilibrium between vanadium and silicon in liquid iron under liquid $FeO–V_2O_3–SiO_2–MgO$ slags. This system is not as suitable for precise thermodynamic deductions as that studied by Dastur and Chipman, because the activities of SiO_2 and V_2O_3 in their slag are not known. It appears, however, that their findings are not in disagreement with those of Dastur and Chipman. The marked influence of vanadium on the activity coefficient of oxygen as shown in Fig. 3, is based on Dastur and Chipman's results. Their deoxidation limits lie well above those which can be calculated from the thermodynamics of V_2O_3[31]

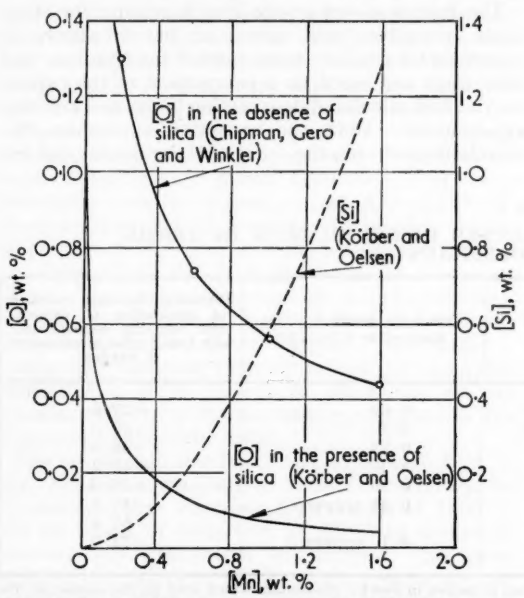


Fig. 9—Deoxidation by manganese at 1600° C. in the presence and absence of silica

and they suggest that the activity coefficient of vanadium in iron may be approx. 0·1. Such a low value for an element similar to iron seems rather unlikely, and the differences may be attributable to errors in the thermal data for V_2O_3.

Other Elements

The deoxidizing powers of a number of other elements were investigated by Oelsen during the last war,[29] but the results have not been published in full. His method was to bring iron melts containing manganese, silicon (and sometimes carbon) and the element under test into equilibrium with silicate slags in silica crucibles at 1600° C. The partition of the various elements between slag and metal was then determined by analysis. An indication of the weight for weight deoxidizing powers of each element in the presence of silica relative to silicon and manganese, was thereby obtained. The results were as follows :

Niobium—rather less effective than manganese
Tantalum—similar to silicon
Molybdenum, *Tungsten*, *Tin*—ineffective, almost entirely reduced from $FeO–SiO_2$ slags to the metal at carbon contents as low as 0·02%.

The Effect of Silicon and Silica in addition to other Deoxidizing Elements

In the simple deoxidation of iron by silicon, the presence of silica causes a lowering of the activity of the ferrous oxide in the slag. For instance, the activity coefficient of ferrous oxide in a ferrous oxide–silica slag at 1600° C., is nearly unity.[30] When saturated with silica, the slag in equilibrium with the iron contains about 48 molar % of ferrous oxide, so that the activity of the latter is about 0·5. The oxygen content of the iron will then be about 0·11%, instead of 0·22% which would be reached in equilibrium with pure ferrous oxide.

If manganese is used as a deoxidizer under such conditions it has been shown by Körber and Oelsen[24] that there still exists an equilibrium of the type

$$(FeO) + [Mn] = [Fe] + (MnO).$$

The value of K_T expressed in terms of concentrations for this reaction is about six times as great with slags saturated with silica, as with pure MnO–FeO slags. The two sets of values taken from Körber and Oelsen's work are as follows :

Temp., ° C.	K_T for Pure Oxides	K_T for Oxides Saturated with Silica
1550	250	1550
1600	200	1200
1650	170	900
1700	140	720

$$\text{where } K_T = \frac{(\text{wt.-\% MnO})[\text{\% Fe}]}{(\text{wt.-\% FeO})[\text{\% Mn}]}$$

Within the likely error limits of Körber and Oelsen's measurements, the above values of K_T are identical with values expressed as molar fractions, on account of the nearly equal atomic weights of iron and manganese. The effect of silica in increasing K_T is in line with the well-known stability of the manganese silicate, rhodonite, and with the instability of the corresponding ferrous compound.

The molar fraction of silica at saturation in MnO–FeO slags is nearly independent of the MnO/FeO ratio, and ranges from 0·54 in the presence of MnO alone to 0·52 in the presence of FeO alone. Since

Körber and Oelsen have obtained reasonably constant values of K_T at any one temperature, it is evident that the activity coefficients of the FeO and the MnO in the presence of the silica are little affected by the proportions of the two oxides present. An activity coefficient of unity may be taken therefore as holding for the FeO in these slags, and the oxygen concentrations in the equilibrium metal may be calculated from the above values of K_T. At 1% [Mn] and 1600° C., for example, the value of [O] in the presence of silica should be about $\frac{1}{9}$ of that in its absence. Some of the oxygen results obtained in the presence of silica by Körber and Oelsen are shown in Fig. 9, together with those calculated for deoxidation by manganese alone from the equation of Chipman, Gero, and Winkler (*see* p. 142). At 1% [Mn] the two oxygen values are 0·007 and 0·056% and the ratio is 1 : 8. The results are in good agreement, especially as no account can be taken of the secondary effects of the dissolved silicon on the activity coefficients of the manganese.

The effect of silica is likely to be of importance in the case of deoxidizers which are less effective than silicon and which form stable silicates. With the elements in normal use the major effect occurs with manganese. Smaller effects are to be anticipated with chromium[25] and vanadium, and virtually none with titanium.

The case of aluminium has been studied by Geller and Dicke[11] who heated melts containing silicon in alumina crucibles. They measured the equilibrium concentrations of [Al] and [Si] in the metal, and the compositions of the slags, which contained about 94% of silica and corresponded closely to the silica–mullite eutectic. The silicon in the metal ranged up to 5% and the aluminium to 0·01%. The equilibrium which Geller and Dicke actually measured may be represented by the equation

$$2(Al_2O_3)_{(\text{in mullite})} + 3[Si] = 3(SiO_2)_{(\text{slag})} + 4[Al].$$

Since the slag was nearly saturated with silica, the activity of the silica in the slag must have been almost that of pure solid silica, at least at the lowest temperature of 1575° C. If the oxygen contents are calculated from silica concentrations using the previously given data of Körber and Oelsen for the equilibrium [Si]–[O]–(SiO_2), the values of the product $[Al]^2[O]^3$ are not very different from the values derived by Geller and Dicke from their melts containing carbon in the absence of silicon. As the activity of alumina in mullite in the presence of silica must almost certainly be low, it appears that silicon does not raise the activity coefficient of aluminium to the same degree as carbon. This is also in line with Geller and Dicke's finding that the constant for their silicon equilibrium hardly changes as the silicon concentration is increased from 2% to 5%.

DISCUSSION

The interactions which occur between liquid iron, dissolved oxygen, and a dissolved alloying element make deoxidation a complex process even in the simplest system. In practice other solutes, such as carbon and silicon, are always present in the iron. In addition the deoxidation products frequently interact with each other and with the refractories, to form complex slags. In contrast, the results discussed in this paper are based on controlled studies of relatively simple systems, so that they cannot be applied rigidly to works conditions. Nevertheless any understanding or explanation of the results obtained in practice should not run counter to the physico-chemical basis outlined above.

The interaction between the various solutes in liquid iron which have been referred to in this paper are summarized in terms of activity coefficients in Table I. The last column gives the *difference* between the energies of association of oxygen with each alloying element (X), and with iron as measured by the function

$$\Delta H_{25^\circ C.}\{X_{(\text{solid})} + \tfrac{1}{2}O_{2(1\,\text{atm.})} = XO_{(\text{solid})}\} - \Delta H_{25^\circ C.}\{Fe_{(\text{solid})} + \tfrac{1}{2}O_{2(1\,\text{atm.})} = FeO_{(\text{solid})}\}$$

The figures shown in the fourth column for chromium, vanadium, and carbon are based entirely on experimental results ; those quoted for titanium and aluminium are based on a comparison of the experimental and calculated deoxidation limits and are only approximate. With the exception of carbon, the correlation between the order of these figures and the

Table I

INTERACTION BETWEEN VARIOUS SOLUTES IN LIQUID IRON IN TERMS OF ACTIVITY COEFFICIENTS

Solute [X]	$\gamma_{[X]}$ at high dilution	Manner in which $\gamma_{[X]}$ is influenced by carbon	Factor by which $\gamma_{[O]}$ is lowered by 0·5% [X]	Difference between energies of association of oxygen with alloying element and with iron, kg.cal./gram-atom of oxygen
Cr	1	Possibly lowered*	0·94	−27·6
Mn	1	Probably lowered†	(0·9)	−30·0
V	Probably 1	...	0·73	−36·9
Si	0·017	raised	(0·8)	−42·2
C	0·61	...	0·70	+35·3
Ti	Probably low	...	0·41 (approx.)	−47·5
B	Probably 0·001	...	...	−57·4
Al	0·025	raised	0·1 (approx.)	−71·0

* This effect is complementary to the lowering of the activity coefficient of carbon in iron by chromium, which may be the reason for the difficulty in removing carbon from ferrochrome.[16]

† Manganese is known to decrease $\gamma_{[C]}$ in solid iron,[21] it is therefore reasonable to expect carbon to decrease $\gamma_{[Mn]}$ in liquid as well as solid iron.

Table II

RESIDUAL OXYGEN IN PRESENCE OF ALLOYING ELEMENT

Deoxidizer	0·01% Alloy		0·10% Alloy		1·0% Alloy		$-\Delta G_{1600^\circ C.}$, kg.cal./gram-atom of oxygen	$-\Delta H_{25^\circ C.}$, kg.cal./gram-atom of oxygen
	1540° C.	1600° C.	1540° C.	1600° C.	1540° C.	1600° C.		
Fe	...	...	...	...	...	...	35·0	62·0
Mn	...	...	0·13	0·18	0·035	0·057	58·5	92·0
Cr	...	...	0·079	0·13	0·031	0·043	50·5	89·6*
V	...	...	...	0·054	...	0·020	62·5	98·9
$Mn(SiO_2)$	...	...	0·035	0·043	0·0055	0·0081	...	...
Si	0·032	0·059	0·010	0·019	0·0032	0·0060	53·0	104·1
C	...	...	0·020	0·022	0·0035	0·0038	66·0	26·7 (CO)
Ti	...	0·015	...	0·0055	...	...	68·0	109·5
Al	0·004	0·01	0·0008	0·002	...	...	85·0	113·0

* The reversal in the order of chromium and manganese is due to the difference in the form of the deoxidation constants ($[Cr]^2[O]^3$ and $Mn][O]$) arising from the difference between the formulae for the two oxides.

order of the energy differences given in the last column is striking. As would be expected, the interaction of an alloying element with dissolved oxygen increases markedly with the heat of formation of its oxide. The figures shown in brackets in the fourth column for manganese and silicon are estimates made on the basis of the correlation. Carbon appears to behave in an anomalous manner, for which it is difficult to find an explanation. It must be admitted, however, that Marshall and Chipman's findings[27] on the manner in which $\gamma_{[O]}$ is influenced by carbon need further substantiation. The effect is not large compared with the experimental errors, and less precise evidence has been cited by Herasymenko[15] for an effect in the reverse direction, *i.e.*, for a *raising* of $\gamma_{[O]}$ by dissolved carbon.

Since carbon is frequently present in systems which are treated with deoxidizers, it is of interest to note the manner in which $\gamma_{[X]}$ is influenced by carbon. It appears that elements which have carbide-forming tendencies but which interact weakly with iron, have their activity coefficients lowered by carbon. Elements which interact more strongly with the iron than with carbon have their activity coefficients raised.

Deoxidation is an essential part of the steelmaking process because the oxygen contents of steel tapped from the furnace are greater than those required on freezing, or those in the final product. According to the practice adopted it is necessary to remove varying proportions of this dissolved oxygen by converting it to oxides which rise from the metal as a separate phase. The proportion removed may be relatively small as in the case of rimming steels, or virtually complete as in dead killed material. The choice of a deoxidizer obviously depends on how low an oxygen concentration it is desired to reach and on the secondary effects of the deoxidizing elements on the properties of the solid metal.

The results calculated here and reported in Figs. 7*a* and *b* are also summarized in Table II which includes the standard free energies of formation at 1600° C. and the heats of formation at 25° C. of the oxide products per gram-atom of oxygen. The more negative the values of $\Delta G_{1600^\circ C.}$ the greater are the deoxidizing powers of the elements concerned : the greater the values of $\Delta H_{25^\circ C.}$ the more markedly does the fall in temperature from 1600° C. to 1540° C. assist deoxidation.

The marked influence of temperature on the deoxidation equilibria indicates that this equilibria must be shifted to lower oxygen concentrations the whole time the metal is cooling in the ladle and the ingot. This shift will, of course, have little effect on the residual oxygen unless the deoxidizer is present at a reasonable concentration. On solidification a further marked increase in deoxidation is to be expected owing to the segregation of both oxygen and deoxidizing elements from the freezing solid into the neighbouring liquid. Even if the metal were in equilibrium just before freezing, the segregation would cause the concentrations of deoxidizer and oxygen to exceed the equilibrium values locally as soon as freezing starts. Oxides will be formed in the neighbourhood of the freezing wall. Whether they are trapped between the dendrites of the freezing metal, or escape and rise to the surface, will depend on such factors as rimming conditions, the shape of the mould, and the rate of freezing. Although deoxidation should in all cases proceed to lower and lower oxygen levels by the cooling of the liquid freezing, and by further cooling in the solid state, the actual quantities of oxides which can separate will be small provided the oxygen concentration has been brought to sufficiently low values at the higher temperatures.

Acknowledgments

The author is indebted to those who criticized this paper, when it was first presented as a lecture at the Steelmaking Conference of the British Iron and Steel Research Association on September 27th, 1949.

References

1. S. L. Case : *Iron Age*, 1949, vol. 164, p. 97.
2. H. M. Chen and J. Chipman : *Transactions of the American Society for Metals*, 1947, vol. 38, p. 70.
3. J. Chipman : *Metal Progress*, 1949, vol. 56, p. 219.
4. J. Chipman : *Discussions of the Faraday Society*, 1948, No. 4, pp. 40, 44, and 46.
5. J. Chipman and K. L. Fetters : *Transactions of the American Society for Metals*, 1941, vol. 29, p. 955.
6. J. Chipman, J. B. Gero, and T. B. Winkler : *Journal of Metals*, 1950, vol. 188, p. 341.

XUM

7. J. CHIPMAN and A. M. SAMARIN : *Transactions of the American Society for Metals*, 1937, vol. 25, p. 331.
8. M. N. DASTUR and J. CHIPMAN : *Discussions of the Faraday Society*, 1948, No. 4, p. 100 ; *Transactions of the American Institute of Mining and Metallurgical Engineers*, 1949, vol. 185, p. 441 ; *Journal of Metals*, 1949, Aug., p. 441.
9. G. DERGE : *Transactions of the American Institute of Mining and Metallurgical Engineers*, 1946, vol. 167, p. 93 ; *Metals Technology*, 1946, vol. 13, Technical Publication No. 2004, Aug. 1946.
10. M. G. FONTANA and J. CHIPMAN : *Transactions of the American Society for Metals*, 1936, vol. 24, p. 313.
11. W. GELLER and K. DICKE : *Archiv für das Eisenhüttenwesen*, 1943, vol. 16, p. 431.
12. M. T. GRANT and J. CHIPMAN : *Transactions of the American Institute of Mining and Metallurgical Engineers*, 1946, vol. 167, p. 134 ; *Metals Technology*, 1946, vol. 13, Technical Publication No. 1988, April 1946.
13. R. W. GURRY : *Transactions of the American Institute of Mining and Metallurgical Engineers*, 1944, vol. 158, p. 101 ; *Metals Technology*, 1943, vol. 10, Technical Publication No. 1641, Dec. 1943.
14. P. HERASYMENKO : Private communication.
15. P. HERASYMENKO : *Discussions of the Faraday Society*, 1948, No. 4, p. 338 ; *Journal of The Iron and Steel Institute*, 1947, vol. 157, p. 515.
16. D. C. HILTY : *Transactions of the American Institute of Mining and Metallurgical Engineers*, 1949, vol. 185, p. 91 ; *Journal of Metals*, 1949, Feb., p. 91.
17. W. JANDER and A. KRIEGER : *Zeitschrift für anorganische Chemie*, 1937, vol. 232, p. 39.
18. W. JANDER and H. SENF : *Ibid.*, 1933, vol. 210, p. 316.
19. K. K. KELLEY : *Industrial and Engineering Chemistry*, 1944, vol. 36, p. 865.
20. K. K. KELLEY : *Bulletin of the United States Bureau of Mines*, 1934, No. 371.
21. K. K. KELLEY : *Ibid.*, 1941, No. 434.
22. K. K. KELLEY : *Ibid.*, 1949, No. 476.
23. F. KÖRBER and W. OELSEN : *Mitteilungen aus dem Kaiser Wilhelm Institut für Eisenforschung*, 1932, vol. 14, p. 181.
24. F. KÖRBER and W. OELSEN : *Ibid.*, 1933, vol. 15, p. 271.
25. F. KÖRBER and W. OELSEN : *Ibid.*, 1935, vol. 17, p. 239.
26. O. KUBASCHEWSKI and O. VON GOLDBECK : *Transactions of the Faraday Society*, 1949, vol. 45, p. 948.
27. S. MARSHALL and J. CHIPMAN : *Transactions of the American Society for Metals*, 1943, vol. 30, p. 695.
28. B. F. NAYLOR : *Journal of the American Chemical Society*, 1946, vol. 68, p. 1077.
29. W. OELSEN : *F.I.A.T. Review of German Science*, 1939–46, *Ferrous Metallurgy*, 1948, vol. 1, p. 20.
30. F. D. RICHARDSON : *Discussions of the Faraday Society*, 1948, No. 4, p. 244.
31. F. D. RICHARDSON and J. H. E. JEFFES : *Journal of The Iron and Steel Institute*, 1949, vol. 163, p. 397.
32. W. A. ROTH and U. WOLF : *Recueil des Traveaux Chimiques des Pays-Bas*, 1940, vol. 59, p. 511.
33. A. M. SAMARIN and A. V. POLIAKOV : Bulletin of the Academy of Science of the U.S.S.R., Section of Technological Science, 1949, p. 100.
34. C. H. SHOMATE : *Journal of the American Chemical Society*, 1947, vol. 69, p. 220.
35. R. P. SMITH : *Ibid.*, 1948, vol. 70, p. 2724.
36. F. E. SYNDER and H. SELTZ : *Ibid.*, 1945, vol. 67, p. 683.
37. C. R. TAYLOR and J. CHIPMAN : *Metals Technology*, 1942, vol. 9, Technical Publication No. 1499, Sept. 1942.
38. B. J. TODD and R. R. MILLER : *Journal of the American Chemical Society*, 1946, vol. 68, p. 530.
39. H. WENTRUP and G. HIEBER : *Archiv für das Eisenhüttenwesen*, 1939–40, vol. 13, p. 15.
40. H. WENTRUP and G. HIEBER : *Archiv für das Eisenhüttenwesen*, 1939–40, vol. 13, p. 69 ; *Technische Mitteilungen Krupp, Forschungsberichte*, 1939, vol. 5, p. 47.
41. T. B. WINKLER and J. CHIPMAN : *Metals Technology*, 1946, vol. 13, Technical Publication No. 1987, April 1946.
42. C. A. ZAPPFE and C. E. SIMS : *Metals Technology* 1942, vol. 9, Technical Publication No. 1498, Oct. 1942.

ADDENDUM*

Since this paper was written, further data on the deoxidation equilibria which involve aluminium, silicon, and manganese have been reported by Hilty and Krafts.† Their results with manganese show oxygen concentrations which are in general lower (between 10 and 50%) than those recommended here on the basis of the equation of Chipman, Gero, and Winkler given on page 142. Their results obtained with silicon agree reasonably well with those of Körber and Oelsen which are referred to on page 142. Results obtained with silicon and manganese together, in equilibrium with slags saturated with silica, agree reasonably with those of Körber and Qelsen, in the range 1·0–0·2% of silicon, but differ at lower silicon concentration. A marked effect of manganese in lowering the oxygen concentrations obtained in the presence of silicon, when the slags are not saturated with silica, was also reported. This is in line with activity coefficients of less than unity for silica and manganese oxide when they form a slag together, and is to be anticipated in view of the remarks on page 143.

Hilty and Krafts' results for aluminium show oxygen concentrations in the liquid iron about three times greater than the accepted results of Wentrup and Heiber (*see* page 141). The author considers that these new results cannot be accepted without further confirmation as it is doubtful whether true equilibria were measured by Hilty and Krafts. They themselves indicate that their liquid and solid deoxidation products contained iron oxides and $FeO.Al_2O_3$, so that it is almost certain that they were not measuring the equilibrium with solid alumina. Equilibrium with a phase containing iron oxide would of course be expected at the higher oxygen and lower aluminium concentrations. It could also lead theoretically to *higher* oxygen concentrations than would be obtained in equilibrium with alumina at low oxygen and high aluminium concentrations. Under the latter conditions, however, such an equilibrium would be metastable and, in the author's view, rather improbable. The suggestion of such an equilibrium also appears to run counter to the existing $FeO–Al_2O_3$ phase diagram.‡

It is the opinion of the author, that there is not at present sufficient case for revising the deoxidation values quoted in this paper.

* Received 27th July, 1950.

† *Journal of Metals*, 1950, vol. 188, pp. 414 and 425.

‡ A. B. McIntosh, J. R. Rait, and R. Hay : *Journal of the Royal Technical College, Glasgow*, 1937, vol. 4, p. 72.

Continuous Temperature Measurement of Liquid Steel in the Furnace

By D. Hardwick, B.Sc., and H. Everard

SYNOPSIS

Continuous records of the temperature of steel in a side-blown converter have been obtained throughout the blowing operation by fitting a Pt/Pt–Rh thermocouple with a specially designed protective sheath into the refractory wall during the lining of the vessel. Results from a number of trials have indicated that this arrangement could be of general application for steel-melting research and possibly for the works control of steelmaking.

Introduction

SCHOFIELD[1] has shown that a platinum/platinum alloy thermocouple gives a reliable measurement of the temperature of liquid steel, provided the thermocouple is protected by a thin-walled silica sheath. The thermocouple, now known as the quick-immersion pyrometer, because it is capable of giving a quick isolated reading of steel bath temperature, has recognized applications for research and works purposes, but it will not withstand steel bath conditions for much longer than a minute. A continuous record of temperature is, however, needed particularly for the converter process because of the speed of the operation and the inaccessibility of the metal during blowing. The arrangement described in this paper is capable of withstanding even the violent agitation of the metal and slag experienced in the side-blown process.

Earlier work of the Side-Blown Converter Practice Sub-Committee[2] indicated the need for thermochemical data on the oxidation of carbon, silicon, etc. Such data have a direct application to the technical control of steel-melting operations, and the present work was carried out with the object of supplying this data.

Early trials confirmed that conditions in a converter were very severe: the thermal shock, slag erosion, and mechanical stress due to the violent agitation of the molten metal bath were great, and the maximum temperatures approached the melting point of platinum (1773° C.). To withstand these conditions the thermocouple was mounted in a refractory sheath built into a position of minimum wear, in the refractory wall of the converter. Such thermocouples have given continuous temperature records for as many as five consecutive blowing operations, representing a life of 2½ hr., before failure. With more experience and development, the life of the thermocouple may be increased still further, but with the converter furnace it is unlikely that a very much greater life can be expected. Considerably longer life should be obtained, however, with other types of furnace, such as the electric-arc and the open-hearth.

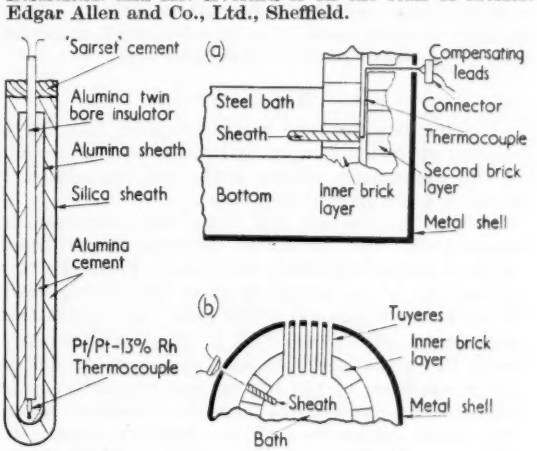
TECHNIQUE

The thermocouple used was of the normal platinum/platinum–13% rhodium type, protected by a composite refractory sheath consisting of an outer fused silica sheath (7 in. × ½ in. × ⅝ in.) into which was inserted a recrystallized alumina sheath (6 in. × ¼ in. × ⅜ in.). The intervening space was packed with dry alumina cement and the whole was sealed with a refractory fire-clay cement, 'Sairset.' The two thermocouple wires were kept separate by insertion in a twin-bore alumina insulator, which was inserted into the inner sheath and embedded in position with dry alumina cement (*see* Fig. 1.). The refractory sheaths were mechanically supported and the heat was more readily conducted to the thermocouple by the dry refractory packing.

During the lining of the vessel the thermocouple was inserted about two-thirds of the way down the metal depth, and about 9 in. from the tuyeres, where it had been shown that the wear on the refractory was least. A hole was cut in the 4½-in. thick inner brick lining, and the thermocouple was inserted, leaving the outer sheath projecting 3 in. into the bath. The leads were taken up through the space between the two brick layers and out to the metal

Paper SC/AA/36/50 of the Melting Sub-Committee of the Steel Castings Division of the British Iron and Steel Research Association, received 15th May, 1950.

Mr. Hardwick is in the Steel Castings Division of B.I.S.R.A. and Mr. Everard is on the staff of Messrs. Edgar Allen and Co., Ltd., Sheffield.



(Fig. 1) *(Fig. 2)*

Fig. 1—Thermocouple arrangement

Fig. 2—Section showing the position of the thermocouple in a steel bath (*a*) vertical, (*b*) transverse

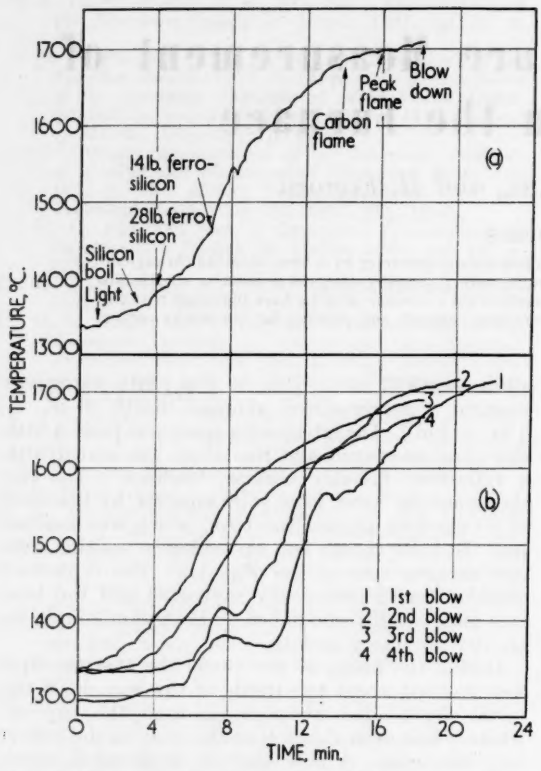


Fig. 3—Temperature/time relationship for (*a*) fourth blowing operation in a newly lined converter, (*b*) four consecutive blowing operations with one thermocouple

shell, where compensating leads were connected rigidly to avoid the possibility of electrical shortening of the thermocouple wires during manipulation of the converter (*see* Figs. 2*a* and *b*).

Preliminary readings were taken with a quick-reading potentiometer; a direct-current amplifier and a high-speed recorder were later used.

RESULTS

The temperature/time relationship for the fourth blowing operation in a newly lined converter, details of the appearance of the bath, and the additions made to it, are given in Fig. 3*a*.

During the carbon boil very little increase in temperature was recorded, although the violence of the reaction suggested otherwise. From the first appearance of the carbon flame to the turning down of the vessel at the end of the blow, the temperature increment rarely exceeded 50° C. This does not necessarily mean that the temperature increment due to the combustion of the carbon was negligible. The bulk of the carbon was probably oxidized before the visible appearance of the boil, as shown (*see* Fig. 4) in earlier work.[3] The addition of ferro-silicon

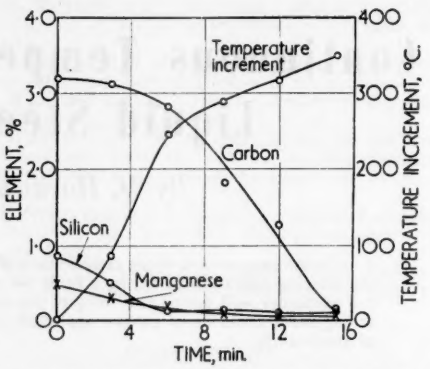


Fig. 4—Graph showing chemical changes in the bath and the temperature increment during the blowing operation

is followed by a sharp temperature rise; the peak of the carbon flame is associated with a steady temperature.

Results obtained during four consecutive blowing operations with one thermocouple prior to its failure, are given in Fig. 3*b*. The curves are typical and show a considerable variation between different blowing operations. Curve 1 shows that there is a tendency for the first blowing operation in a newly lined vessel to be associated with an initial lag in temperature rise, which is compensated for later by a very rapid temperature increase.

CONCLUSIONS

The extended use of an immersion thermocouple to give a continuous recording of the temperature in steel-melting baths is now a practical possibility. The arrangement has been tested only on side-blown converter furnaces, but since the operating conditions on a side-blown converter are extremely severe, it might reasonably be expected that with slight modifications the technique will prove applicable to any steel-melting furnace.

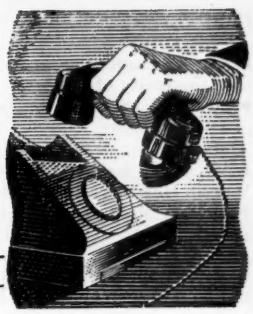
Apart from the works control application of this technique, it should prove valuable in supplying further information on the changes occurring during the steel-melting process, and further work in this direction is now in hand.

The authors wish to thank their colleagues for assistance and encouragement in various ways, particularly Messrs. A. J. Langner and A. Searby of B.I.S.R.A. and Mr. H. S. Mason of Messrs. Edgar Allen and Co., Ltd., in whose works many of the tests have been carried out.

References

1. F. H. SCHOFIELD: Seventh Report on the Heterogeneity of Steel Ingots, *Special Report No.* 16, p. 222: 1937. The Iron and Steel Institute.
2. First Report of the Side-Blown Converter Practice Sub-Committee: *Journal of The Iron and Steel Institute*, 1947, vol. 155, pp. 33–50.
3. J. L. HARRISON, W. C. NEWELL, and A. HARTLEY: *Journal of The Iron and Steel Institute*, 1948, vol. 159, pp. 281–290.

NEWS



ANNOUNCEMENTS AND NEWS OF SCIENCE AND INDUSTRY

THE IRON AND STEEL INSTITUTE

Symposium on High-Temperature Steels and Alloys for Gas Turbines

It has been found necessary to postpone the Symposium which had been arranged to take place on Wednesday and Thursday, 18th and 19th October, 1950.

The Fifth Hatfield Memorial Lecture, which was to be held in association with the Symposium, is also postponed.

Furthur details of the revised arrangements for the Meeting will be given later.

NEWS OF MEMBERS

▶ Mr. B. R. BANERJEE, research engineer in the Engineering Research Division of the Standard Oil Company, Chicago, has been awarded the degree of Doctor of Engineering of Yale University.

▶ Mr. G. J. BANNER has been appointed Works Metallurgist of the Aston Chain and Hook Co., Ltd., Birmingham.

▶ Mr. W. R. BERRY, Consulting Engineer and Metallurgist, has been awarded the Ph.D. degree of the University of Leeds.

▶ Mr. U. G. BHAT has left the Indian Smelting and Refining Co., Ltd., Bombay, and is studying for the degree of Master of Metallurgical Engineering at the University of Lehigh, Bethlehem, U.S.A.

▶ Mr. B. F. BROWN has been awarded the degree of Doctor of Science, and has left the Massachusetts Institute of Technology to join the Department of Engineering Research at the North Carolina State College.

▶ Mr. D. C. BROWN has left the General Electric Company, Ltd., to take up an appointment as metallurgist with Rotol's Ltd., Gloucester.

▶ Mr. R. A. CRESSWELL has left the Tin Research Institute, Greenford, to take up an appointment as Research Metallurgist with the British Oxygen Co., Ltd., Morden, Surrey.

▶ Major H. B. DESHPANDE of the Department of Metallurgy, B.N. Railway, Kharagpur, has been nominated by the Government of India as a member of the reconstituted Metals Research Committee, for three years.

▶ Mr. M. F. DOWDING has been appointed Engineering Sales Manager of Davy and United Engineering Co., Ltd. Until recently Mr. Dowding was Rolling Mill Research Engineer, and has just returned from an extended tour of the U.S. steel industry. He is a member of the Rolling Committee of the British Iron and Steel Research Association.

▶ Mr. R. DUTT has joined the Group Establishment of Messrs. Martin Burn, Ltd.

▶ Dr. K. L. FETTERS, Special Metallurgical Engineer at the Youngstown Sheet and Tube Company, Ohio, has been appointed assistant to the Vice-President in charge of operations.

▶ Mr. H. A. HOARE has been appointed research metallurgist with Aluminium Laboratories, Ltd., Banbury.

▶ Mr. S. T. JAZWINSKI has left the Barium Steel Corporation to take up an appointment as Senior Staff Engineer in the Metallurgical Department of the Ford Motor Co., Detroit.

▶ Mr. W. B. KEITH has left Messrs. Wm. Beardmore and Co., Ltd., to join the staff of Messrs. Edgar Allen and Co., Ltd., Sheffield.

▶ Mr. E. KULA has left the Royal Technical University, Stockholm, to enter the graduate school of the Massachusetts Institute of Technology.

▶ Mr. R. F. MCGAVIN has left the Panteg Works of Messrs. Richard Thomas and Baldwins, Ltd., to take up an appointment as Technical Assistant to the Directors, and Head of the Laboratories of the Exors. of James Mills, Ltd., Bredbury Steel Works and Rolling Mills, Woodley, nr. Stockport.

▶ Mr. J. B. MCINTYRE, Senior Lecturer at the National Foundry College, Wolverhampton, has been awarded the M.Sc. degree of the University of London.

▶ Mr. J. A. MACMILLAN has been appointed Assistant Superintendent of the Jackson Iron and Steel Co., Jackson, Ohio, U.S.A.

▶ Mr. B. K. MAHENDRA, Managing Partner of Messrs. Mecanico, New Delhi, has been awarded the Fellowship of the Geological Mining and Metallurgical Society of India.

▶ Mr. H. B. MYERS has left the Roll Manufacturers Institute and has been appointed Metallurgical Engineer with the S. H. BELL Company, Pittsburgh, U.S.A.

▶ Major A. C. G. PENNA has joined the New York branch of the Brazilian National Steel Company.

▶ Mr. V. A. PHILIPS has been awarded the degree of Doctor of Engineering of Yale University.

▶ Mr. A. PRINCE has transferred from I.C.I. General Chemicals Division to the Fertiliser and Synthetic Products Division at Billingham.

▶ Professor A. G. QUARRELL has been appointed to the Chair of Metallurgy at Sheffield University.

▶ Mr. S. J. RAMAGE has taken up an appointment with the Indian Copper Corporation, Chota Nagpur.

▶ Mr. W. J. S. ROBERTS, Head of the Research Department of the Ebbw Vale Works of Messrs. Richard Thomas and Baldwins, Ltd., has been appointed Chief Metallurgist at the New Cold Reduction Plant and Tinplate Works of the Steel Company of Wales, at Trostre.

▶ Mr. K. W. Rowe has left the Broken Hill Pty. Co., Ltd., to take up an appointment with Gunnersen Allen Metals Pty., Ltd., Melbourne, Australia.

▶ Mr. K. SACHS has been awarded the M.Sc. degree of the University of London.
▶ Dr. R. W. SANDEL has been appointed Chief Metallurgist with Messrs. Connors Steel Company, Birmingham, Alabama.
▶ Mr. H. S. SASTRI has left the Mysore Iron and Steel Works, Bhadravatai, India.
▶ Dr. W. M. S. WALKER has been appointed Technical Director of the Round Oak Steel Works, Ltd., Brierley Hill, Staffs.
▶ Mr. F. T. WHEELWRIGHT has joined the staff of the Midland branch of Messrs. Richard Thomas and Baldwins Ltd.

Obituary

Dr. H. W. GILLETT, formerly Director of the Battelle Memorial Institute, Columbus, on 3rd March, 1950.

Col. Sir W. CHARLES WRIGHT, Bt., G.B.E., C.B., Past-President of the Institute, on 14th August, 1950.

CONTRIBUTORS TO THE JOURNAL

J. E. Wells, B.Sc., A.R.I.C., A.Met.—Research Chemist and Metallurgist at The Steel Company of Wales (Lysaght Works) Ltd. Mr. Wells received his technical education at the University of Sheffield where he obtained the Associateship in Metallurgy in 1942. In 1945 he was awarded a B.Sc. degree (honours in chemistry) of London University, and in the same year he was granted an Associateship of the Royal Institute of Chemistry.

He gained his first industrial experience in the Brown-Firth Research Laboratories, firstly in the pyrometry and chemical laboratories, and later in the gases and inclusions laboratory, where he specialized in research on gases in steel and micro-chemical analysis. He took up his present appointment in 1947.

Mr. Wells is a member of the Gaseous and Non-Metallics Sub-Committee and of the Solid Steel Study Groups and the Nitrogen Study Group of the British Iron and Steel Research Association.

IRON AND STEEL ENGINEERS GROUP

The **Fourteenth Meeting** of the Group will be held in London on Tuesday, 5th December, 1950. The programme will include the presentation and discussion of a paper "*Hot Bloom and Slab Shears*," by J. A. Kilby (Colvilles Ltd.), and a paper "*Electric Drives for Reversing Hot Mills*," by P. E. Peck (B.T.H. Co., Ltd.).

Further details of the meeting will be published later.

AFFILIATED LOCAL SOCIETIES

Sheffield Metallurgical Association

A joint Meeting of the Sheffield Metallurgical Association and The Iron and Steel Institute will be held at the Grand Hotel, Sheffield, on the evening of Tuesday, 21st November, 1950, at 7.0 P.M. Dr. J. White, President of the Association, will be in the Chair.

Professor A. Preece, of King's College, Newcastle-upon-Tyne, will give a lecture on "The Overheating of Steel."

BRITISH IRON AND STEEL RESEARCH ASSOCIATION

Physics Laboratories

To mark the Third Anniversary of the Official Opening of the Laboratories, Open Days will be held on 9th and 10th November, 1950.

EDUCATION

National Certificates in Metallurgy

REPORT BY THE JOINT COMMITTEE ON THE PROGRESS OF THE SCHEME FOR THE AWARD OF NATIONAL CERTIFICATES IN METALLURGY FOR THE YEAR 1948–1949

Schemes for courses leading to National Certificates in Metallurgy have been in operation during 1948–1949 at the following Technical Colleges:

Ordinary Certificate—Battersea Polytechnic, London; Birmingham Central Technical College; Chesterfield Technical College; Corby Monotechnic Institute; Coventry Technical College; Cumberland Technical College, Workington; Derby Technical College; Enfield Technical College; Leeds College of Technology; Merchant Venturers' Technical College, Bristol; Middlesbrough, Constantine Technical College; Neath Mining and Technical Institute; Newport Technical College, Monmouthshire; Nottingham and District Technical College; Rotherham College of Technology; Scunthorpe Technical School; Shotton, Deeside Technical Institute; Smethwick, The Chance Technical College; Stoke-on-Trent, North Staffordshire Technical College; Swansea Technical College; Wednesbury, County Technical College; Wolverhampton and Staffordshire Technical College.

Contributory Centres — Bordesley Green Technical School and Moseley Grammar School Evening Institute (Contributory Centres to Birmingham Central Technical College); Dudley and Staffordshire Technical College (Contributory Centre to Wednesbury, County Technical College); Nottingham People's College Senior Technical Institute (Contributory Centre to Nottingham and District Technical College).

Higher Certificate—Battersea Polytechnic, London; Birmingham Central Technical College; Chesterfield Technical College; Coventry Technical College; Middlesbrough, Constantine Technical College; Rotherham College of Technology; Rugby College of Technology; Smethwick, The Chance Technical College; Swansea Technical College; Wednesbury, County Technical College; Wolverhampton and Staffordshire Technical College.

In 1949 final Examinations for the Ordinary National Certificate were held at 21 Technical Colleges, and for the Higher National Certificate at 10 Technical Colleges, for candidates who satisfied the conditions laid down in Ministry of Education Rules 111, under which the scheme is operated.

106 Candidates have qualified for the award of an Ordinary National Certificate in Metallurgy, and 50 candidates have qualified for the award of a Higher National Certificate, as a result of Final Examinations held in 1949. The records of a further 2 candidates for the Ordinary National Certificate have been approved by the Joint Committee, subject to the fulfilment of certain conditions. One candidate for the Ordinary National Certificate and 9 candidates for the Higher National Certificate who entered the Final Examinations in 1948 and whose records were approved by the Joint Committee, subject to certain provisions, have qualified for the award of Certificates in 1949. Distinctions have been gained by 44 candidates who have shown an exceptional grasp of their subjects, indicating a high degree of training and knowledge in the particular subject in which the Distinction has been gained.

Comparative figures of entries and successful candidates for the four years since the institution of the Scheme for National Certificates in Metallurgy are as follows:

Ordinary Certificate

Year	Technical Colleges	Number of Candidates Entered	Awarded Certificates
1946	4	28	23
1947	11	102	69
1948	15	123	74
1949	21	222	107*

* Including one candidate whose Certificate was withheld in 1948

Higher National Certificate

Year	Technical Colleges	Number of Candidates Entered	Awarded Certificates
1946	...	...	...
1947	2	22	18
1948	8	38	22
1949	10	74	59*

* Including nine candidates whose Certificates were withheld in 1948

Prizes were awarded to 48 successful candidates who have shown particular merit in the Final Examinations in 1949, from the Prize Fund established for this purpose by The Iron and Steel Institute, the Institution of Mining and Metallurgy, and the Institute of Metals.

The Joint Committee is pleased to note the increase in the number of Technical Colleges holding Final Examinations in 1949, and in the number of candidates entering for the examinations ; also the continued increase in the number of students entering the first and second years of the courses.

The Joint Committee welcomes the setting up of a Committee, and the institution in 1948–49, of a Scheme for the award of National Certificates in Metallurgy in Scotland.

The following candidates successfully completed the senior part-time course for the year 1948–49 and have been awarded the Ordinary National Certificate in Metallurgy ; a subject given in parentheses indicates the award of a distinction in that subject :

ORDINARY CERTIFICATE

Battersea Polytechnic, London—Bangay, Alan John ; Bridges, Dennis Francis Wm. (introductory metallurgy (physical), chemistry) ; Humphries, Jean Mary ; Nabbs, Stanley William ; Scott, Dudley John ; Wilson, Richard Joseph ; Wood, Barrie ; Woods, Arthur George Wm.

Birmingham Central Technical College—Broomfield, Geoffrey Hugh (engineering drawing) ; Clare, Eric Samuel ; Deville, Arthur Ernest ; Gallimore, Peter William (engineering drawing) ; Hatcher, George Clarence ; Hall, Brian William ; Jones, Ronald Arthur Charles ; Murcott, Arthur William ; Rees, Benjamin Lewis ; Reeves, Gordon Leonard ; Rigby, June Curtis ; Rollestone, Arthur William ; Swann, Brian ; Warrington, Peter ; Wood, Allan ; Woolley, Alfred Trevor (general metallurgy).

Chesterfield Technical College—Clayton, Alan ; Orme, John Percival (physical chemistry) ; Salt, Norman ; Stock, Donald Calthorpe (physical chemistry) ; Stockton, Keith John ; Waterhouse, Roy (physical chemistry).

Corby Monotechnic Institute—Pentelow, John Eric ; Roe, Kenneth Frank ; Shadbolt, Ronald Wm. (physics).

Coventry Technical College—Boston, Stanley John ; Durrant, Philip Ernest ; Ford, Ashley Gregg ; Jordan, Douglas Arthur ; Spriggs, Geoffrey Edwin (general metallurgy).

Cumberland Technical College, Workington—Armstrong, William ; Baggley, Thomas (metallurgy) ; Orr, Thomas Frederick ; Sandelands, Alan ; Straughton, Leslie Buchanan (physics, metallurgy).

Derby Technical College—Hitchen, Howard J. (physical chemistry) ; MacLaine, Colin R. (metallurgy) ; Paxton, Peter R.

Enfield Technical College—Atkins, John William ; Cox, Antony Hugh ; Lucey, Victor Francis.

Middlesbrough, Constantine Technical College—Stott, Peter Rowland.

Neath Mining and Technical Institute—Hughes, Owen David ; Jones, David Henry ; Parry, Joseph Desmond ; Thomas, Alwyn John Pugh (general metallurgy).

Newport Technical College—Fowler, Basil Stanley ; Jones, Derrick ; Price, William George.

Nottingham and District Technical College—Blake, A. R. (physics) ; Hampson, Terence Gilbert ; Large, Michael John.

Rotherham College of Technology—Marvill, Geoffrey ; Pallister, Donald ; Wigfield, Kenneth (inorganic and physical chemistry) ; Williams, John Kirkby.

Scunthorpe Technical College—Nicholson, Anthony (physics, metallurgy) ; Oliver, George Richard.

Shotton, Deeside Technical Institute—Ash, Arthur ; Barnes, John Roy ; Cork, John Samuel ; Dolan, Terence Peter ; Edwards, Owen Mervyn ; Pratt, Kenneth Graham ; Sharpe, Edgar Charles.

Smethwick, The Chance Technical College—Bailey, Leslie William ; Brookshaw, Clement William ; Cheesman, George Dean ; Griffin, Keith Henry ; Webb, Ronald James (qualified for an endorsement in foundry practice).

Stoke-on-Trent, North Staffordshire Technical College—Barks, Reginald Wm. ; Bond, Leslie James ; Flower, Stewart Arthur ; James, David Francis (physical chemistry) ; Jones, Ivan ; Rogers, Thomas Sydney ; Small, Edward Charles ; Swinson, Wilfred.

Swansea Technical College—Amphlett, David C. J. (chemistry, general metallurgy) ; Cunniffe, Peter Wm. Arthur (chemistry, general metallurgy) ; Grinter, Eric James ; Hooper, Elston Frank ; Lewis, Gerald Ivor ; Leyshon, Gwendoline Joan (general metallurgy) ; Parry, Raymond ; Rees, Arthur (chemistry, physics) ; Rowlands, Francis Victor ; Smith, Leonard George ; Snook, Vivian Thomas James (general metallurgy) ; Thomas, John Malcolm (chemistry, general metallurgy) ; Williams, John Morley ; Williams, Thomas Gwyn.

Wednesbury County Technical College—Greenshill, Alfred Vincent ; Harper, Cecil Trevor ; Jones, Stanley Raymond Dennis ; King, Hubert Wylam (qualified for supplementary endorsement in welding) ; Marsters, Edgar Alan ; Neu, Max Gerhardt ; Phillips, Arthur James.

HIGHER CERTIFICATE

The following candidates successfully completed the advanced part-time course for the year 1948–49, and have been awarded the Higher National Certificate in Metallurgy ; a subject given in parentheses indicates the award of a distinction in that subject :

Battersea Polytechnic, London—James, Victor Leonard ; Proffitt, Henry Joseph ; Sheppard, Norman Frederick.

Birmingham Central Technical College—Burnard, David Chance ; Dunning, Malcolm John ; Lee, Raymond Frederick ; Pester, Dorothy Margaret (iron and iron alloys II) ; Storer, Roy Alan ; Thomas, John Leslie ; Toach, Shirley Alan.

Chesterfield Technical College—Meakin, John ; Moss, John Barry (metallurgical analysis, treatment of ferrous metals and alloys) ; Pugh, Jack Fisher.

Coventry Technical College—Heritage, Stanley John ; Wood, Brian Ernest.

Middlesbrough, Constantine Technical College—Blackburn, Keith (foundry technology) ; Brownlee, Malcolm (metallurgy, metallurgical analysis) ; Burn, Alan Hall (physical metallurgy) ; Dale, Alan ; Franks, Osmond ; Gill, Everard Reginald (metallurgical analysis) ; King, Arthur Edward (foundry technology) ; McArdle, Gordon

Dickinson ; McDonald, Raymond ; Nash, Russell Reginald (metallurgy) ; Richardson, Henry Kenneth. (K. Blackburn has qualified for supplementary endorsement in foundry technology (distinction), mineral dressing, working treatment, and testing of metals ; Arthur Edward King has qualified for supplementary endorsement in foundry technology (distinction), and mineral dressing.)

Rotherham College of Technology—Graves, Geoffrey Basil (qualified for supplementary endorsement in metallurgical analysis) ; Concannon, William (production of iron and steel).

Smethwick, The Chance Technical College—Allen, Gordon Leonard (principles of physical metallurgy, treatment of ferrous metals and alloys, manufacture and treatment of non-ferrous metals and alloys) ; Brett, Alan Samuel (manufacture and treatment of non-ferrous metals and alloys) ; Forsyth, Richard Victor Walter (principles of physical metallurgy, manufacture and treatment of non-ferrous metals and alloys, treatment of ferrous metals and alloys) ; Greensmith, Joseph Frederick ; Hayward, Brian Philip ; McManus, William George (principles of physical metallurgy, manufacture and treatment of ferrous metals and alloys, manufacture and treatment of non-ferrous metals and alloys) ; Moore, Harold ; Peyton, Benjamin Alfred (treatment of ferrous metals and alloys, manufacture and treatment of non-ferrous metals and alloys) ; Salmon, Clifford Gerald (principles of physical metallurgy, manufacture and treatment of non-ferrous metals and alloys, treatment of ferrous metals and alloys) ; White, John Harold (principles of physical metallurgy, manufacture and treatment of non-ferrous metals and alloys). G. L. Allen and W. G. McManus have qualified for supplementary endorsement in manufacture and treatment of non-ferrous metals and alloys ; R. V. W. Forsyth and C. G. Salmon have qualified for supplementary endorsement in treatment of ferrous metals and alloys ; B. A. Peyton has qualified for supplementary endorsement in manufacture and treatment of non-ferrous metals and alloys.

Swansea Technical College—Lewis, Ogwyn (metallurgical analysis) ; Rees, George Philip (metallurgical analysis).

Wednesbury County Technical College—Feasey, Raymond J. ; Hanson, Cedric Charles ; Meadows, Albert A. ; Smith, Kenneth Arthur ; Strathearn, Alfred A. ; Tranter, Norman (metallurgical analysis) ; Tyler, Anthony W. (metallurgical analysis) ; Wakeman, Peter J. C. C. Hanson and K. A. Smith, and Betty Doo and G. Winfield who gained Certificates in 1948, have qualified for supplementary endorsement in extraction and refining of common non-ferrous metals.

Wolverhampton and Staffordshire Technical College—Bull, Stanley Ivor ; Crowe, Stanley Frederick ; Fisher, Kevin ; Green, John Redmond ; Head, Harold Edward (metallurgical analysis) ; Holgate, Sheila Marjory ; Meachem, Frederick Arthur ; Myatt, Ronald Tom ; Richards, Charles John Godfrey ; Sheward, George Edward ; Williams, John Randall.

Prizes

Prizes have been awarded to the following candidates in respect of the Final Examinations for Ordinary and Higher National Certificates in Metallurgy for the year 1948–49 :

Battersea Polytechnic, London—Bridges, Dennis Francis William (three guineas).

Birmingham Central Technical College—Broomfield, Geoffrey Hugh (one guinea) ; Gallimore, Peter William (one guinea) ; Pester, Dorothy Margaret (one guinea) ; Woolley, Alfred Trevor (two guineas).

Chesterfield Technical College—Moss, John Barry (four guineas) ; Orme, John Percival (one guinea) ; Stock, Donald Calthorpe (three guineas) ; Waterhouse, Roy (one guinea).

Corby Monotechnic Institute—Pentelow, John Eric (one guinea) ; Shadbolt, Ronald William (one guinea).

Coventry Technical College—Spriggs, Geoffrey Edwin (two guineas).

Cumberland Technical College, Workington—Baggley, Thomas (one guinea) ; Straughton, Leslie Buchanan (four guineas).

Derby Technical College—Hitchen, Howard J. (two guineas) ; MacLaine, Colin R. (one guinea).

Middlesbrough, Constantine Technical College—Blackburn, Keith (1 guinea) ; Brownlee, Malcolm (four guineas) ; Burn, Alan Hall (three guineas) ; Gill, Everard Reginald (one guinea) ; King, Arthur Edward (one guinea) ; Nash, Russell Reginald (one guinea).

Neath Mining and Technical Institute—Thomas, Alwyn John Pugh (two guineas).

Newport Technical College—Jones, Derrick (one guinea).

Nottingham and District Technical College—Blake, Alan Richard (two guineas).

Rotherham College of Technology—Concannon, William (one guinea) ; Wigfield, Kenneth (two guineas).

Scunthorpe Technical School—Nicholson, Anthony (three guineas).

Shotton, Deeside Technical Institute—Barnes, John Roy (one guinea).

Smethwick, The Chance Technical College—Allen, Gordon Leonard (three guineas) ; Brett, Alan Samuel (one guinea) ; Forsyth, Richard Victor Walter (three guineas) ; McManus, William George (five guineas), Peyton, Benjamin Alfred (two guineas) ; Salmon, Clifford Gerald (five guineas).

Stoke-on-Trent North Staffordshire Technical College—James, David Francis (three guineas).

Swansea Technical College—Amphlett, David Charles Josiah (four guineas) ; Cunniffe, Peter Wm. Arthur (four guineas) ; Lewis, Ogwyn (one guinea) ; Leyshon, Gwendoline Joan (one guinea) ; Rees, Arthur (four guineas) ; Rees, George Philip (one guinea) ; Snook, Vivian Thomas James (one guinea) ; Thomas, John Malcolm (four guineas).

Wednesbury County Technical College—Tranter, Norman (one guinea) ; Tyler, Anthony W. (two guineas).

Wolverhampton and Staffordshire Technical College—Head, Harold Edward (one guinea) ; Williams, John Randall (one guinea).

NEWS OF SCIENCE AND INDUSTRY

Graduate Courses at Birmingham

Graduate courses in Mechanical Engineering, Chemical Engineering, and Metallurgy will be given in the Faculty of Sciences of the University of Birmingham during the session 1950–51 (session begins 2nd October, 1950). The fee for each course will be £70, including lecture, laboratory examination, and membership fees. Applications should be addressed to the Registrar, The University, Edgbaston, Birmingham, 15.

The Course in Metallurgy covers the following studies : Structural Metallurgy ; Industrial Metallurgy ; Principles of Refining, Melting, and Casting ; Principles of the Working of Metals, Heat-Treatment, and Welding ; Modern Laboratory Techniques.

The Scientific Instrument Manufacturers' Association of Great Britain, Ltd.

At the Council meeting following the Thirty-third Annual General Meeting of this Association, held on

Thursday, 13th July, 1950, the following officers were elected for the year 1950–51 :

President :	M. H. Taylor
Vice-Presidents :	J. E. C. Bailey, C.B.E.
	A. W. Smith
Hon-Treasurer :	S. Borthwick
Hon. Secretary :	J. Rock Cooper

The Universities and Industry

A party of University teachers from Oxford, Cambridge, and Sheffield, was entertained by The United Steel Companies, Limited, during the week ending July 15th. Three days were spent in visiting steelworks in Sheffield and Scunthorpe and in discussions with the Company's staff.

The idea of trying this experiment came from the F.B.I. Conference on relations between Industry and the Universities which was held last November at Ashorne Hill.

Discussions ranged over a wide field and included the Company's organization, which was explained by the Managing Director, Mr. Gerald Steel. Mr. A. J. Peech, the Deputy Managing Director, lead a discussion on problems affecting the steel industry as a whole.

News from Spain

Many who attended the Institute Special Summer Meeting in Norway last year will be interested to learn of the marriage, on August 2nd, 1950, of Señorita Paloma, daughter of the Marqués de Triano, to Mr. Glen Collins, of the United States Diplomatic Service. A week before the ceremony Major W. R. Brown was present at a charming gathering of relatives and friends ; he conveyed to the bride the felicitations of her many friends in the Institute. This luncheon party was held in a delightful lake-side chalet, the interior decorations of which have been carried out in exquisite taste by Señorita Carmen Goyoaga, who also will be remembered by many on the Norwegian trip.

Powder Metallurgy

The Metal Powder Association, New York, have published the Proceedings of the Sixth Annual Meeting, held in Detroit in conjunction with the Metal Powder Show, at $2.50 per copy.

The Association have also issued the following standards :

M.P.A. Standard 8-50T. "Acceptance Tests on Structural Parts made from Metal Powders," which describes tests for a variety of pressed and sintered parts

M.P.A. Standard 9-50T, "Definitions of Terms Used in Powder Metallurgy "

M.P.A. Standard 10-50T. "Standard Tension Test Specimens for Pressed and Sintered Metal Powders."

Copies may be obtained at 25 cents per copy.

Company Changes

RICHARD THOMAS AND BALDWINS, LTD., and The Steel Company of Wales, Ltd., announce the formation of a Company which will act as the organization for the effecting and carrying through of the export sales of mild steel flat-rolled products manufactured by them and their respective subsidiaries.

The Company was registered on the 10th July, 1950, with a nominal share capital of £1000. The Directors of the new Company are Mr. H. F. Spencer (Chairman), Joint Assistant Managing Director of Richard Thomas and Baldwins, Ltd., and Mr. E. Julian Pode, Managing Director of The Steel Company of Wales, Ltd.

The Secretary of the Company is Mr. J. Idris Roberts. The Registered Office of the Company is at 47 Park Street, London, W.1.

SIR GEORGE GODFREY and PARTNERS, LTD., of Hampton Road, Hanworth, Middlesex, have undertaken a major reorganization in the structure of the Company, by forming three new Companies, Sir George Godfrey and Partners (Holdings), Ltd., which is the financial controlling company, with two subsidiaries, Sir George Godfrey and Partners, Ltd., who will continue to specialize in aircraft pressurization and air conditioning equipment, and Sir George Godfrey and Partners (Industrial), Ltd., which has been formed to undertake the industrial interests of the Company.

Change of Address

THE REPUBLIC STEEL CORPORATION have closed their London office and all communications should be sent to their Export Office, 9th Floor, Chrysler Building, 230 Lexington Avenue, New York.

DIARY

18th Oct.—SOCIÉTÉ FRANÇAISE DE MÉTALLURGIE—Centenary Celebrations of the birth of Henri de Chatelier—Paris.

19th–27th Oct.—AMERICAN SOCIETY FOR METALS—32nd National Metal Congress and Exposition—Chicago.

23rd–27th Oct.—AMERICAN SOCIETY FOR METALS—Fifth Annual Metallographic Exhibit—Chicago.

23rd–25th Oct.—INTERNATIONAL CONFERENCE ON THE STUDY AND UTILIZATION OF SLAGS—Brussels.

TRANSLATION SERVICE

(The previous announcement was made in the September, 1950, issue of the *Journal*, p. 92.)

TRANSLATIONS AVAILABLE

No. 406 (German). A. E. LENDL : "Bevelling and Rounding-off in Roll-Pass Design." (*Stahl und Eisen*, 1949, vol. 69, Apr. 28, pp. 306–308).

No. 407 (Czech). J. FORMÁNEK : "Development of the Briquetting of Lignite and Coal without Admixture of a Binder and Description of the New Briquetting Process for Coal and Lignite without a Binder by the 'Dolní-Rychnov Method.'" (*Bánský Obzor*, 1949, vol. 3, July, pp. 97–99 ; Aug., pp. 121–123).

No. 408 (Spanish). F. MILLAN and F. BARBADILLO : "The Sintering and Preparation of Iron Ores at the Vizcaya Works of the Altos Hornos de Vizcaya, S.A." (*Instituto del Hierro y del Acero (Journal)*, 1950, vol. 3, No. 1, Jan./Mar., pp. 47–53). (Abridged translation prepared by Mr. R. Sewell and made available through the courtesy of the Research and Development Department, The United Steel Companies, Ltd., Stocksbridge, near Sheffield).

CHARGES FOR COPIES OF TRANSLATIONS—The charge for the above translations is £1 for the first copy and 10*s*. for each additional copy of the same translation. Requests should be accompanied by a remittance. These translations are not available on loan from the Joint Library.

TRANSLATIONS PREPARED AT MEMBERS' REQUEST—Members requiring translations of foreign papers are invited to communicate with the Secretary, who will ascertain whether they can be prepared for inclusion in the Series.

ABSTRACTS OF CURRENT LITERATURE *and* BOOK NOTICES

IRON AND STEEL MANUFACTURE AND RELATED SUBJECTS

CONTENTS

	PAGE
ORES—MINING AND TREATMENT	154
FUEL—PREPARATION, PROPERTIES, AND USES	154
REFRACTORY MATERIALS	155
BLAST-FURNACE PRACTICE AND PRODUCTION OF PIG IRON	155
DIRECT PROCESSES	155
PRODUCTION OF STEEL	156
FOUNDRY PRACTICE	156
HEAT-TREATMENT AND HEAT-TREATMENT FURNACES	157
FORGING, STAMPING, DRAWING, AND PRESSING	158
ROLLING-MILL PRACTICE	158
LUBRICANTS AND LUBRICATION	158
WELDING AND FLAME-CUTTING	158
MACHINING AND MACHINABILITY	159
CLEANING AND PICKLING	160
PROTECTIVE COATINGS	160
POWDER METALLURGY	160
PROPERTIES AND TESTS	160
METALLOGRAPHY	163
CORROSION	163
ANALYSIS	164
HISTORICAL	165
ECONOMICS AND STATISTICS	165
MISCELLANEOUS	166
BOOK NOTICES	166
NEW PUBLICATIONS	168

ORES—MINING AND TREATMENT

Manufacture of Nodules from Fine Ore and Limestone at Buffalo, N.Y. A. A. Oesterle. (American Institute of Mining and Metallurgical Engineers, Blast Furnace, Coke Oven and Raw Materials Conference, 1949 Proceedings, vol. 8, pp. 132–138). A description is given of the equipment and process adopted when a cement works with two rotary kilns was converted to produce iron ore nodules from fine ores and limestone. The kilns were 11 ft. in dia. and 175 ft. long with a slope of 1 in 24. The burner pipes were increased from 10 to 14 in. in dia. and the velocity of the air carrying the pulverized fuel was considerably reduced. The nodules were heated to 2250–2400° F. and the kiln rotated at 48 r.p.hr. About 205 lb. of fuel were consumed per 2000 lb. of nodules, and each kiln produced 700–750 short tons of nodules per day.—R. A. R.

Manufacture of Nodules at Ironton, Ohio, Using Mesabi Fines and Blast-Furnace Flue Dust. E. F. Brownstead. (American Institute of Mining and Metallurgical Engineers, Blast Furnace, Coke Oven and Raw Materials Conference, 1949 Proceedings, vol. 8, pp. 139–145). The paper describes how a cement works changed over their kilns to the manufacture of nodules from a 50/50 mixture of blast-furnace flue dust and iron ore fines. There were six rotary kilns, and one of these, with a diameter of 7 ft. at the discharge end, was used for the initial tests. From the experience gained the author recommends that if a new kiln were built for this purpose it should be 10–11 ft. in dia. in the burning zone and 150 to 175 ft. long.—R. A. R.

Operation and Practice, Producing Iron Sinter at Ducktown and Copperhill, Tennessee, with Fine Flotation Sulphides. R. R. Burns. (American Institute of Mining and Metallurgical Engineers, Blast Furnace, Coke Oven and Raw Materials Conference, 1949 Proceedings, vol. 8, pp. 146–157). The Tennessee Copper Company, having developed a selective flotation process for the treatment of ores containing sulphides of copper, iron, and zinc, commenced sintering the iron concentrate in 1925 to produce a sinter with 68–69% of iron and only 1–2% of silica. The concentrate is a raw material for the production of sulphuric acid as well as for sinter. It is first roasted, which removes 80% of the sulphur as SO_2, and in the subsequent sintering the remaining iron sulphide provides the fuel. The plant and some results obtained are described.—R. A. R.

Briquetting Fine Ores at Woodward, Alabama. H. A. Byrns. (American Institute of Mining and Metallurgical Engineers, Blast Furnace, Coke Oven and Raw Materials Conference, 1949 Proceedings, vol. 8, pp. 158–170). The author reports trials in the production of briquettes from iron ore fines and blast-furnace flue dust with binders such as cement, bentonite, and cereals. Two Komareck-Greaves briquette presses with a combined capacity of about 60 tons/hr. of briquettes are in use. The charging of briquettes and other improvements to blast-furnace practice have reduced the average flue dust per gross ton of pig iron from 117 lb. in 1943 to 54 lb. in 1948.—R. A. R.

Ore Mining and Blending for Geneva Steel Company. C. L. Waggoner. (American Institute of Mining and Metallurgical Engineers, Blast Furnace, Coke Oven and Raw Materials Conference, 1949 Proceedings, vol. 8, pp. 172–192). The mining and crushing operations at Iron Mountain, Utah, and the ore bedding and Robins-Messiter ore-reclaiming systems at the Geneva steelworks are described and illustrated.

Ore Blending. R. R. Williams, jun. (American Institute of Mining and Metallurgical Engineers, Blast Furnace, Coke Oven and Raw Materials Conference, 1949 Proceedings, vol. 8, pp. 193–203). The crushing, screening, sintering, blending, and reclaiming of iron ore by the Colorado Fuel and Iron Corporation are described. Two Dwight-Lloyd sintering machines and the Robins-Messiter system of reclaiming are employed.—R. A. R.

Ore Blending as Practised by the Kaiser Company and the Kaiser and Frazer Parts Corporation. E. J. Duffy. (American Institute of Mining and Metallurgical Engineers, Blast Furnace, Coke Oven and Raw Materials Conference, 1949 Proceedings, vol. 8, pp. 204–210). The ore-blending systems at Ironton, Utah, the mining at Eagle Mountain, and piling and reclaiming at Fontana, Calif. are described.—R. A. R.

Ore Blending by Tennessee Coal, Iron and Railroad Company. F. H. Crockard. (American Institute of Mining and Metallurgical Engineers, Blast Furnace, Coke Oven and Raw Materials Conference, 1949 Proceedings, vol. 8, pp. 211–227.) The ore-conditioning and sintering plant of the Tennessee Coal, Iron and Railroad Company, Bessemer, Alabama, is described and illustrated. Blending is done on the basis of excess acidity so that all blends shall require the same amount of fluxing stone at the blast-furnace. Coarse ore (over $1\frac{1}{16}$ in.) is stored in 20 silos, each with a capacity of about 820 tons of red ore, and medium ore ($\frac{1}{4}$ to $1\frac{1}{16}$ in.) in 20 silos of the same size. The silos are divided into groups of four and each of the four discharge on to the same proportional feeder. The gates of these silos and the proportional feeders are remote controlled from a control room. The sintering plant for the fines consists of three 72-in. wide Dwight-Lloyd machines with auxiliary equipment.—R. A. R.

FUEL—PREPARATION, PROPERTIES, AND USES

Reducing Coal-Expansion Pressure. C. C. Russell, M. Perch, and J. F. Farnsworth. (American Institute of Mining and Metallurgical Engineers, Blast Furnace, Coke Oven and Raw Materials Conference, 1949 Proceedings, vol. 8, pp. 32–50).

The causes of the pressure exerted by the charge in coke ovens have been studied. The conclusions were : (1) Reducing the bulk density of the charge is an effective means of reducing the pressure ; this also reduces the oven capacity and, if a faster coking time is attempted to compensate this, the expansion increases again. (2) The fluidity of the coal during coking can be increased, with consequent reduction of the pressure, by additions of coke breeze, low-temperature coke, oxidized coal, anthracite fines, and sawdust. (3) A layer of coke breeze on top of the charge prevents the formation of a pressure peak near the end of the carbonizing period. (4) The effect of oven width on the pressure is more apparent in widths up to 12 in., and is negligible with widths over 12 in. (5) The existence of a plastic envelope in the oven has been demonstrated and measures which prevented its formation reduce the pressure on the oven walls.—R. A. R.

New Design of Equipment for Recovery of Ammonium Sulphate and Light Oil. H. Otto. (American Institute of Mining and Metallurgical Engineers, Blast Furnace, Coke Oven and Raw Materials Conference, 1949 Proceedings, vol. 8, pp. 50–60). New designs of saturator in which coke-oven gas is bubbled through ammonium sulphate liquor containing free sulphuric acid are described ; these were designed with the object of reducing high pressure differences. One design has a round mouthpiece to the immersed gas inlet, which is flared at an angle of 11° and has slots and serrations at the outer edges. Another design, with a pressure resistance below 9 in. water gauge, was constructed to deal with a gas flow of 100 million cu. ft. of gas per day ; in this, the ammonia was removed by spray nozzles. Light oil scrubbers are also described.—R. A. R.

The Rehabilitation of Coke Ovens by Hot-Repair Methods. E. Preston, A. C. Sedlachek, W. C. Wardner, and S. H. Kimmel. (American Institute of Mining and Metallurgical Engineers, Blast Furnace, Coke Oven and Raw Materials Conference, 1949 Proceedings, vol. 8, pp. 61–83). It is shown that a coke-oven battery gradually deteriorates to a certain critical condition after which the deterioration rate rises sharply to the point of oven failure. Consequently repair work before the critical state is reached is advocated on the principle that it is easier to hold brickwork together than to rebuild it. Special techniques for repairing buckstays, 'through walls,' tops, and flues are described, some of these being for repairs while the ovens are hot.—R. A. R.

Rebuilding Old Coke Ovens. F. L. McIntirc. (American Institute of Mining and Metallurgical Engineers, Blast Furnace, Coke Oven and Raw Materials Conference, 1949 Proceedings, vol. 8, pp. 84–93). The repair programme and the techniques employed at three coke-oven batteries (two Koppers and one Wilputte) of the Jones and Laughlin Steel Corporation are described.—R. A. R.

Rebuilding and Repair of Old Ovens. W. D. Spaulding. (American Institute of Mining and Metallurgical Engineers, Blast Furnace, Coke Oven and Raw Materials Conference, 1949 Proceedings, vol. 8, pp. 94–96). Repairs to coke ovens at the works of the Weirton Steel Company since 1937 are briefly described.—R. A. R.

Repairs to Coke Ovens, Alan Wood Steel Company. P. C. Mayfield. (American Institute of Mining and Metallurgical Engineers, Blast Furnace, Coke Oven and Raw Materials Conference, 1949 Proceedings, vol. 8, pp. 97–100). The repair techniques employed on two batteries of Koppers cross-regenerative coke ovens built in 1919, and one battery of Koppers-Becker ovens built in 1929 are briefly described.
R. A. R.

REFRACTORY MATERIALS

Reactions in the Solid State at High Temperature of Mixtures of Refractory Oxides of the Systems Cr_2O_3–MgO–FeO, Al_2O_3–TiO_2, Cr_2O_3–TiO_2. Miss M. Hamelin. (Société Française de Métallurgie, Oct. 6, 1949 : Revue de Métallurgie, Mémoires, 1950, vol. 47, Apr., pp. 324–328). Mixtures of the oxides were heated to temperatures between 1000° and 1500° C. ; for those containing FeO a reducing atmosphere was used, but the others were heated in air. The analyses of the products were derived from X-ray diffraction diagrams obtained by the powder method. The compounds produced are described and discussed.—A. E. C.

Cupola Linings. M. Guédras. (Métallurgie, 1949, vol. 81, Nov., pp. 17, 19). A brief survey is presented of the nature of cupola linings, the action of the constituent elements of slags on the linings, the composition of various lining materials, the process of lining a cupola, and the use of stabilized dolomite as a lining material.—J. C. R.

BLAST-FURNACE PRACTICE AND PRODUCTION OF PIG IRON

Practical Aspects of the Manufacture of Pig Iron in the Coke Blast-Furnace. J. J. Welter. (Ciencia e Tecnica, 1949, Oct., pp. 198–224). [In Spanish]. The author surveys, in general terms, the technical and economic aspects of iron manufacture in the modern coke blast-furnace producing 1000 to 1500 tons/day. The dependence of the blast-furnace on coke quality is the only shadow on the efficiency and economy of the classical process of pig-iron manufacture. Evidence as to the possibilities of other methods, more adaptable to existing raw materials, can be drawn from the lessons learned in the development of modern blast-furnace practice.

The author describes the design of a modern blast-furnace and the typical layout of a blast-furnace plant. He discusses the heat balance, but does not enter into details of the chemical reactions of the process. The economy of the blast-furnace is discussed in terms of the fuel and ore factors, cost of refractories, air, cooling, and calculation of depreciation.

Recent developments, including ore preparation, oxygen-enriched blast, and high top pressure, are discussed. He concludes with the questions : " Why make so many efforts to adapt raw materials to the metallurgical process ? Why not accommodate the process to the raw materials ? " and feels that this latter approach might be well worth while in countries not favoured by nature in the matter of raw materials.
R. S.

The Possibilities of the Production of High Quality Pig Iron in Brazil. D. Pospeloff. (Mineração e Metalurgia, 1949, vol. 14, Nov.–Dec., pp. 6–7). [In Portuguese]. The author concludes that it is possible to produce high-quality pig iron in Brazil in blast-furnaces and in electric furnaces.

The old method of charcoal burning at the sites where timber is cut must be abandoned in favour of the new method of producing charcoal in furnaces. The ash, phosphorus, and sulphur contents of the charcoal must be specified in relation to the different kinds of trees used and the varying thickness of trunk. The metallurgical industry must finance research on sintering. More careful research into iron and manganese ore deposits and limestone must be carried out.—R. S.

The Desulphurization of Iron. J. Vibrac. (Métallurgie, 1949, vol. 81, Oct., pp. 19–21, Nov., pp. 13–15). A review of the work of various investigators on the desulphurization of iron from the blast-furnace is presented.—J. C. R.

DIRECT PROCESSES

On the Direct Reduction Processes of Iron Ores with Special Reference to the Availability of Iron Scrap. F. Árkos. (Bányászati és Kohászati Lapok, 1949, vol. 4, Sept., pp. 376–381). [In Hungarian]. The Högenäs, Kalling, Wiberg, Norsk Staal, Krupp-Renn, Stürzelberg, De Vecchis, and the Basset direct-reduction processes are described and their economy reviewed. Although the technical problems of direct reduction have been solved, it is still necessary to produce steel in two stages. The value of the product obtained by direct methods has, therefore, to be compared with that of iron scrap, not steel.

Before 1939 the average composition of the charges used in Hungary for steel production was : Inland scrap 6–8%, steelworks scrap 25–28%, imported scrap 13–15%, pig iron 50–55%. Of the enumerated processes only the Basset and the Krupp-Renn processes are worth considering for production on an appreciable scale in Hungary. The Basset process is economically justified only if there is a market for the cement produced. The coal consumption is 500 kg./ton for heating, and 372 kg. for chemical reaction per ton of iron produced. A Basset furnace was in operation in Moncada (Spain) producing 80 tons of cement and 50 tons of iron (carbon 0·2–1·2%) per 24 hr. More recently a Basset furnace has been put into operation by the Schmidt cement works, Copenhagen, and special quality pig iron is produced there. The Krupp-Renn process is not suitable for Hungarian charges because they are too high in copper, arsenic, sulphur, and phosphorus. It is proposed to investigate the economics of the Krupp-Renn process for processing imported ores and imported pulverized coke.—E. G.

Production of Sponge Iron in Sweden. F. A. de Toledo Piza. (Mineração e Metalurgia, 1949, vol. 14, Nov.–Dec.,

pp. 1–4). [In Portuguese]. This is a description of the well-known Höganas and Wiborg processes for the manufacture of sponge iron. The advantages and disadvantages of each process are clearly summarized.

It is difficult to say whether the process would be generally useful in Brazil. Due to the enormous size of the country, and the varying conditions from region to region, each case would have to be studied separately, but, in view of the good results obtained in Sweden, it does merit the careful study of Brazilian metallurgists.—R. S.

PRODUCTION OF STEEL

Some Recent Contributions to the Evolution of Iron and Steel Techniques. R. Perrin. (Mémoires de la Société des Ingénieurs Civils de France, 1948, Sept., pp. 624–636). A survey is presented of recent trends in iron and steel production methods in France.—J. C. R.

Oxygen Enrichment of the Blast for the Basic-Bessemer Converter. L. Marbais, A. Grosjean, G. Hotat, M. Poverman, and P. Coheur. (I.R.S.I.A. : Comptes Rendus de Recherches, 1949, No. 1, Nov., pp. 9–53). Complete details are given of works experiments on the use of oxygen-enriched blast in the operation of the basic-Bessemer converter; some were made with scrap additions, whilst in others ore was added. From the steelmaker's point of view, the steels produced were equal to ordinary basic-Bessemer steels; the advantage of the process was the great reduction of cost due to the conversion of a considerable tonnage of scrap into steel. By continuing the enrichment of the blast till conversion was finished, the economic advantages were retained while the steel quality improved, owing to the diminution of the nitrogen and phosphorus contents. When using ore additions along with oxygen-enriched blast the economy was not so good, but the nitrogen content of the steel was as low as that of open-hearth steel. The large amount of heat available makes the process very flexible, so that physically or chemically 'cold' irons can be treated, or the technique can be varied in order to reduce the phosphorus and sulphur contents to the level of open-hearth steel.—A. E. C.

Fundamentals of Flow in Industrial Furnaces. M. Hansen. (Iron and Steel Institute, 1950, Translation Series, No. 400). This is an English translation of a paper which appeared in Archiv für das Eisenhüttenwesen, 1949, vol. 20, Nov.–Dec., pp. 337–344 (*see* Journ. I. and S.I., 1950, vol. 165, June, p. 234).

Control of the Melting of Steel in Open-Hearth Furnaces. I. Danihelka. (Rozpravy Svazu Horních a Hutnických Inženýrů, 1949, vol. 3, pp. 1–155). [In Czech]. The first part of this paper deals with theoretical problems of the production of mild steel and deoxidation. The second part describes the conditions in two different steelworks and compares the methods used and results obtained. In one of the steelworks the charges used were of high carbon content (ore method), whilst in the other very low carbon charges were used (scrap or duplex process). The author's conclusions are: (1) The optimum rate of decarburization of soft rimming steel for deep-drawn sheets or wire is 0·25 to 0·50% carbon/hr. (2) The FeO content of a bath does not increase with increasing rates of decarburization. (3) Too low a rate of decarburization is therefore more harmful than one which is too high. (4) Deep-drawn sheets and soft wire from steel produced by the 'ore' method from liquid pig iron and a high-carbon charge with a decarburization rate of 0·40% carbon/hr. were better than those produced from steel obtained by the 'scrap' process from a low-carbon charge and a decarburization rate of 0·18% carbon/hr. (5) The latter steel improved with increasing carbon in the charge and increasing rate of decarburization. (6) Steels produced from a 'soft' charge with a low decarburization rate became hard easily and cracked during cold shaping, *i.e.*, they aged quickly. (7) Analysis of the conditions during the melting process and the properties of the steels obtained have shown that the main reason for ageing is the FeO content. (8) Although, according to certain authors, the solubility of FeO in iron does not change below the A_1 point, its presence is likely to increase the solubility of other oxides, *e.g.*, MnO, which forms solid solutions with FeO over a wide range of composition. (9) The use of FeO also increases the strength of the steel in the as-cast condition. (10) The strength of soft carbon steels decreases to a certain minimum with decreasing carbon content, *e.g.*, 0·06% for open-hearth steel, 0·05% for basic-Bessemer steel; with further fall in the carbon content the strength increases again owing to increasing FeO content. (11) In reaction with FeO, manganese cannot deoxidize the steel bath late in the heat in the presence of an oxidizing slag, because its deoxidizing effect is less than that of carbon and, in effect, the total oxygen content of the steel is increased by adding manganese in the presence of an oxidizing slag. Graphs are included which give the quantities of manganese, silicon, chromium, phosphorus and sulphur during the melting process, and also the quantities of aluminium to be added to deoxidize rimming steels and the silicon–aluminium to be added for deoxidizing killed steels.—E. G.

Another Look at the Problem of Steel Deoxidation. J. Chipman. (Metal Progress, 1949, vol. 56, Aug., pp. 211–221). The action of deoxidizers is either to diminish the amount of oxygen dissolved in the steel or to render that which is present less active. A review is presented of experimental work over the last 20 years on the steelmaking reactions resulting from the addition of various deoxidizing elements. Data are summarized in the form of a deoxidation equilibrium diagram.—J. C. R.

Alloy Recovery—Chromium Reduction and Recovery from Scrap or Ore in Basic Openhearth. C. R. Funk. (Metal Progress, 1949, vol. 56, Oct., pp. 486–487). When chromium-contaminated scrap was used in the basic open-hearth furnace only 18–28% of the chromium was recovered, the balance being lost as Cr_2O_3 in the slag. As a result of experiments it was found possible to reduce the Cr_2O_3 in the slag to metallic chromium which migrated back to the metal bath. In this way the recovery of chromium exceeded 70%. The practice involved a controlled charge so as to obtain the desired lime, silica, iron oxide, and low slag volume, and a method of slag development by the addition of deoxidizers such as lime, silicon, aluminium, carbon, and fluorspar so as to obtain reactions which result in the ultimate reduction of the Cr_2O_3. In the working period of the slag, basicity and bath temperature are gradually increased and the iron oxide is kept low and often reduced. A reboil is used at the proper time to assist in maintaining a high temperature. The slag additions are made in such a manner that most of the Cr_2O_3 reduction occurs after the reboil. The method has also been used successfully with chrome ore.—J. C. R.

Quality of Oxygen-Decarbonized Acid Electric Steel. C. A. Faist and C. Wyman. (Journal of Metals, 1949, vol. 1, Oct., pp. 18–27). The authors have investigated the many metallurgical factors influencing the quality of oxygen-decarburized acid electric steel. These include: (1) Melt-down carbon concentration, (2) melting rate, (3) total points of carbon removal, (4) rate of carbon removal, (5) melt-down silicon concentration, (6) percentages of FeO, MnO, and SiO_2 in final slag, (7) ratio of acid to basic constituents in final slag, (8) percentage of residual aluminium (total), (9) percentage of manganese recovery (based on additions), (10) time of heat (power on to power off) and (11) tapping temperatures.

FOUNDRY PRACTICE

Distribution of Molten Grey Iron in Foundries. M. Skála. (Hutnické Listy, 1949, vol. 4, Dec., pp. 398–399). [In Czech]. The application of the Gantt diagram for cupola operation for planning the distribution of molten grey iron to the individual casting shops and also for controlling the composition of the cupola charges is discussed.—E. G.

Ferrous Melting Furnaces in the United States and Canada. A. W. Gregg. (International Foundry Congress 1949: Metalen, 1950 Congress Number, Part I, pp. 31–54: American Foundryman, 1949, vol. 16, Oct., pp. 27–32). *See* Journ. I. and S.I., 1950, vol. 165, May, p. 110.

Influence of Knock-Out Temperature on the Graphitization in the Solid State of White Cast Iron. G. Joly. (Fonderie, 1949, Sept., pp. 1725–1728). An account is given of an attempt to determine the effect of knock-out temperature of white-iron castings on the time of decomposition of cementite and pearlite on subsequent annealing. Test pieces were cast and knocked out of the mould at various temperatures. They were then packed with silica sand in iron tubes, heated to 920° C. in 24 hr., kept at that temperature for 25 hr., then cooled to 720° C. in 12 hr. Specimens were withdrawn at intervals after reaching 920° and after cooling to 720° C., and examined by means of micrographs. Knock-out temperature was found to have no effect unless at a high (cherry-red) temperature. In that case a noticeable reduction in

the time required for decomposition of cementite was observed, but the duration of the second stage of graphitization was not affected.—J. C. R.

Fifty Years of Steel Foundry Practice. C. Didierjean. (Fonderie, 1949, Sept., pp. 1729–1739). An account is given of steel foundry practice before 1900 together with a description of a steel foundry of that time. Changes that have taken place and possible developments are surveyed.—J. C. R.

Steel Foundries in Great Britain. C. J. Dadswell. (Fonderie, 1949, Oct., pp. 1763–1782). After reviewing generally developments in steel casting practice in Britain, the author examines various aspects of the methods employed and compares them with those adopted in the United States and European countries. These include mould and core-making practice, cleaning of castings, internal organization of foundries, and the organization of the industry as a whole. J. C. R.

Defects in Large Pulleys. H. Gernelle and P. Nicolas. (Fonderie, 1949, Sept., pp. 1744–1746). Defects in large pulleys may be attributable either to a lack of permeability in the sand when casting or to the composition of the iron used being unsuitable. Practice that will eliminate defects due to the former cause is outlined, and the importance of the sulphur/manganese ratio in the iron is stressed.—J. C. R.

Production Casting 30-Ton Engine Bases. C. W. Gilchrist. (Iron Age, 1950, vol. 165, Mar. 2, pp. 81–85). The casting of a 30-ton engine base for a natural-gas compressor is fully described. The preliminary model was cast in a pit in the foundry floor, and was beyond the capacity of the foundry crane to pull out: later production was therefore made with the bottom drag set in a shallow pit, the cheek section moulded in a flask, and a cope. Sandslingers were used for filling the patterns: about 100 tons of cores were required.—J. P. S.

On the Theory of Degassing Molten Metals. J. Verö. (Bányászati és Kohászati Lapok, 1949, vol. 4, Nov., pp. 473–483). [In Hungarian]. The influence of the temperature and pressure on the quantity of occluded gas, particularly hydrogen, is described, and various methods of degassing are examined. The methods employed were: (1) Solidification of the melt in a hydrogen-free atmosphere; (2) keeping the metal molten in a hydrogen-free atmosphere; (3) purging the melt with an insoluble gas; and (4) degassing under vacuum. Diffusion is not taken into consideration although it has a definite influence in methods (2) and (4).—E. G.

Notes on the Organisation and Control of Production of Castings. D. Iturrioz. (Metalurgia y Electricidad, 1949, vol. 13, Aug., pp. 22–24; Oct., pp. 26–28; Dec., pp. 43–45; 1950, vol. 14, Jan., pp. 19–22). [In Spanish]. Attention is drawn to the importance of drawings, tolerances, patterns, moulds, and surface appearance in the inspection of castings. The course of inspection is outlined and the chain of responsibility is indicated. The writing of inspection and rejection reports is dealt with. The author makes a simple statement of what inspection involves, and describes the usual types of defect encountered. Finally, he considers the reaction of labour to payment by time and by results, and examines a time-study system.—R. S.

HEAT-TREATMENT AND HEAT-TREATMENT FURNACES

The Influence of Some Additions on the Carburization Rate of Steels by Charcoal. J. Doškář. (Hutnické Listy, 1949, vol. 4, Nov., pp. 345–351; Dec., pp. 389–391). [In Czech]. A series of tests was carried out with various carburizing mixtures to find a suitable one which does not contain barium carbonate. Na_2CO_3 was dissolved in distilled water and the solution absorbed by charcoal which was then dried. It was found that mixtures containing 10, 8·5, and 6% Na_2CO_3 have a corrosive effect on the steel surface, and that there is practically no difference in the rate of carburization, and that a 3% Na_2CO_3 mixture gives uniform and equivalent carburization and has no corrosive effect on the parts. The specimens were all from one heat for each type of steel and the charcoal was a representative sample. The carburization tests were carried out in an electric furnace at 880° C. The carbon contents at depths increasing in stages of 0·1 mm., using sodium, potassium, and lithium carbonates with and without stabilizers, are given in tables. The tests showed that charcoal impregnated with barium compounds plus stabilizers made a very good carburizing compound, also that 5% of barium compound is sufficient when combined with sodium salts. A mixture of beryllium and sodium compounds is very effective, and a mixture of cobalt and sodium salts proved suitable for rapid carburizing.—E. G.

Gas Carburizing. C. H. Leland. (Metal Progress, 1949, vol. 55, June, pp. 811–815). The fundamentals of gas carburizing are discussed, and particular consideration is given to the 'tightness' of furnaces, the qualities of the ideal gas, furnace operation, uniformity and measurement of case depth, and the use of a sufficient quantity of gas to ensure maximum carburizing rate without causing excessive sooting in the furnace.—J. C. R.

Furnace Management—Modern Continuous Furnace for Heat-Treatment Used as a Gas Carburizer. T. B. Morris. (Metal Progress, 1949, vol. 56, Oct., pp. 501–503). An account is presented of the gas-carburizing of oil field tools in a pusher-type, gas-fired radiant-tube furnace. The furnace was originally intended only for heat-treatment purposes, but it was found to be suitable for hardening as well, and to possess advantages over the pot-carburizing process. The cost of carburizing was reduced and the performance of the finished products has been satisfactory.—J. C. R.

The Kryptol Electric Furnace. J. Bernot. (Journal du Four Electrique, 1949, vol. 58, Sept.–Oct., pp. 111–113). Kryptol electric furnaces, which are mainly used in laboratories, have some industrial applications where a simple small electric furnace is required, for such purposes as melting salts for salt baths and melting small quantities of high-speed steels. The operation of these furnaces is described.—R. F. F.

Improved RF Induction Heating Cuts Processing Costs. H. C. Dustman. (Steel, 1949, vol. 125, Oct. 17, pp. 72–75). The author describes the types of equipment used for generating high-frequency current for induction heating: Motor generators, spark-gap oscillators and vacuum tube oscillators. The first, operating up to 9600 cycles/sec. are most useful for deep heating, the others, covering a range of 200,000–450,000 cycles, give less penetration and are therefore more useful where surface effects are required. Some features of the design of commercial oscillator tubes are then described.—J. P. S.

The Problem of Hardening Steel, Especially the Kinetics of the Transformations. F. Wever. (Max-Planck-Institut für Eisenforschung Report No. 499: Stahl und Eisen, 1949, vol. 69, Sept. 15, pp. 664–670). Previous investigations of the kinetics of the transformation of austenite, by the Kaiser-Wilhelm-Institut für Eisenforschung are critically reviewed. There are 32 references.—R. A. R.

Variations in the Quenching Power of Salt Baths. A. M. White. (Metal Progress, 1949, vol. 56, Nov., pp. 819–824). It is shown that the quenching power of a low-temperature salt bath consisting of potassium nitrate 53%, sodium nitrite 40%, and sodium nitrate 7% is significantly changed by the presence of small amounts of impurities. The addition of 0·5% of sodium chromate considerably increases the hardness of 0·5% carbon steel specimens quenched in this mixture for 30 sec. at 350° F. and then air-cooled. Contamination by chlorides of alkali metals and alkali earth metals carried over from austenitizing baths causes a decrease in the quenching power.—R. A. R.

Cyanide Hazards. R. H. Duguid and W. C. Cox. (Metal Progress, 1949, vol. 56, Dec., pp. 814–815). The dangers involved in the handling of cyanide salts and the operation of cyanide heat-treatment baths are outlined, and the symptoms and treatment of cyanide poisoning are described.—R. A. R.

Flame Hardening—Selective Flame Hardening Machine for Tractor Gears Results in Economy and a Better Product. A. E. Anderson and R. H. Lundquist. (Metal Progress, 1949, vol. 56, Oct., pp. 506–508). A flame-hardening machine for tractor gears has been designed to replace the quench and temper methods. The following advantages are claimed: (1) Distortion is minimized, hardness at the wearing surfaces is much higher, strength at the root of the teeth is higher, service performance is improved; (2) less capital outlay on equipment is required; (3) the flame-hardening machine can be used for other parts besides gear wheels; and (4) production flows at a smoother rate.—J. C. R.

Annealing for Machinability—Isothermal Treatment of X4340 Increases Furnace Capacity 56%. K. Midlam. (Metal Progress, 1949, vol. 56, Oct., pp. 504–505). Ordnance gear rings were made from W.D. 4640 steel and it was necessary to change to W.D. X4340 steel, but difficulties in machining

XUM

due to hard spots were encountered. Variations were made in the heat-treating cycle until a microstructure of fine carbide spheroids, fine lamellar pearlite, and blocky ferrite was obtained—an ideal structure for machinability. The new procedure effected a considerable saving in time equivalent to a furnace capacity increase of 56%.—J. C. R.

Slack Quenching *versus* Quench Cracking. J. B. Caine and R. S. Haught. (Metal Progress, 1949, vol. 56, Sept., pp. 361–366, 391). The effect of slack quenching (a form of slow quenching) on the mechanical properties of steel is discussed. It is suggested that unless high hardness for wear resistance is required, or high strength dependent on high hardness, slack quenching should be permitted for almost all steel castings, plain or alloyed, since better impact values can be obtained than after an oil or water quench and subsequent annealing.
J. C. R.

FORGING, STAMPING, DRAWING, AND PRESSING

Drop Forge Dies—Hard Chromium Plating Cuts Costs of Die Sinking. S. L. Scheier and R. E. Christin. (Metal Progress, 1949, vol. 56, Oct., pp. 492–494). An account is given of the deposition of hard chromium on the face of drop-hammer forging dies so that wear resistance can be increased, die life extended, and flash line thickness controlled. Only those dies should be chromium plated which are giving excess wear at the flash line and where the design is such that the cost of one sinking is equal to or greater than, the cost of at least two platings.—J. C. R.

250-ton Horizontal Press. J. Willey. (Welder, 1949, vol. 18, July–Sept., pp. 55–56). A 250-ton press has been recently designed and constructed by W. H. Allen, Sons and Co. Ltd., Bedford. Except for the hydraulic ram and cylinder, construction was entirely by welding, from steel plate up to $1\frac{1}{2}$ in. in thickness.—J. P. S.

Progressive Stamping Dies—Dies for Deep Drawn Objects Designed by Unfolding Final Shape. J. F. Tyrrell. (Metal Progress, 1949, vol. 56, Oct., pp. 494–496). A method of multi-stage drawing for difficult parts, such as exhaust systems for aircraft engines, is described. The object is to reduce the number of stages and intermediate annealing. From the final shape, a plaster pattern is prepared in the usual way. This pattern is covered with a water-soluble slip coat. Molten beeswax and cheesecloth are then applied in successive layers until about $\frac{1}{16}$ in. thick. When this replica of the desired shape is cool and stiff, it is readily removed from the plaster by lifting the edge and allowing water to dissolve the slip coat. It is next unfolded or flattened sufficiently to reproduce the penultimate stage of pressing, and held in that position by clay bolsters until it has been backed with about 20 in. of plaster reinforced with jute fibre ; when this has set, it constitutes a matrix for the penultimate dies. The beeswax pattern can then be unfolded a stage further and another plaster matrix prepared. Dies for stainless steel sheet and other alloys difficult to draw have been successfully made by this method.—R. A. R.

Researches on the Deep-Drawing Process. S. Fukui. (Bulletin of the Institute of Physical and Chemical Research, vol. 20, No. 9, pp. 641–680). [In Japanese].

ROLLING-MILL PRACTICE

Present Day Trends in American Rolling Mill Practice. Hauth. (Centre de Documentation Sidérurgique, Circulaire d'Informations Techniques, 1949, vol. 6, June–July, pp. 303–321). This is a report by a French metallurgist of a visit to a number of American steel plants in which he surveys current American rolling-mill practice and technique and gives descriptions of some typical mills.—J. C. R.

Permali Bearings. Edelboude. (Centre de Documentation Sidérurgique, Circulaire d'Informations Techniques, 1949, vol. 6, June–July, pp. 321–322). Permali bearings are made of compressed thin (1–2 mm.) layers of wood impregnated with a phenolic resin, and are used in rolling-mill practice at the Pompey Works in France. A note is given on their properties and the advantages gained by using them.—J. C. R.

Rod and Billet Mill. (Iron Age, 1949, vol. 164, Sept. 15, pp. 78–79). **New Rod Mill To Increase Production at Colorado Fuel and Iron Corp.** (Steel, 1949, vol. 125, Oct. 24, pp. 58–60, 82). **New Rod Mill at Minnequa Works of the Colorado Fuel and Iron Corporation Ready for Operation.** (Blast Furnace and Steel Plant, 1949, vol. 37, Nov., pp. 1319–1326, 1344). **C.F. and I. Rod Mill Speeds Production.** (Iron and Steel Engineer, 1949, vol. 26, Dec., pp. 108–112). **Forty-Six Years of " Know-How " Built into the New Colorado Fuel and Iron Rod Mill at Pueblo.** (Wire and Wire Products, 1950, vol. 25, Mar., pp. 211–215). Descriptions are given of the new rod mill of the Colorado Fuel and Iron Corporation at Minnequa Works, Pueblo, Colorado. (*See* Journ, I. and S.I., 1950, vol. 165, June, p. 240).

Production of Seamless Steel Pipe and Tubes. B. Bannister. (Steel, 1949, vol. 125, Oct. 17, pp. 86, 88, 91, 94, 96 ; Oct. 24, pp. 68–76). The manufacture of seamless steel pipe is described, from piercing, plug rolling, and reeling, to final cooling. A continuous tube rolling mill is also described.—J. P. S.

Source of Error in the Measurement of the Thickness of Sheets with a Flying Micrometer. A. Carlander. (Industritidningen Norden, 1949, vol. 77, Feb. 23, p. 51 : Bulletin d'Information et de Documentation de l'Association Technique de l'Acier et des Métaux Non Ferreux, 1949, vol. 3, Dec., pp. 43–44). When a flying micrometer is used to measure the thickness of sheet or strip between the final pair of rolls and the take-up reel, errors will be introduced as the quantity on the reel increases and the length of strip between the rolls and the reel ceases to be horizontal. Methods are given for calculating these errors.—R. F. F.

LUBRICANTS AND LUBRICATION

Activated Lubricants for the Cold-Drawing of Tubes. V. F. Maltsev, F. M. Gertsman and M. P. Zheldak. (Bulletin d'Information et de Documentation de l'Association Technique de l'Acier et des Metaux Non-Ferreux, 1950, vol. 4, Feb., pp. 22–28). This is a French translation of an article which appeared in the Russian journal " Stal," 1948, No. 2, pp. 147–152. (*See* Journ. I. and S.I., 1948, vol. 159, July, p. 333).

Drawing Die Lubricant—An Efficient Phosphating Compound Preparatory to Cold Drawing of Steel Tubing. J. C. Heymann. (Metal Progress, 1949, vol. 56, Oct., pp. 497–498). Tests are reported on a phosphatizing compound ' Banox,' which is a dry hygroscopic compound composed mainly of aluminium joined to a phosphate radical which (in aqueous solution) produces an amorphous vitreous coating on clean pickled steel. Approximately 3·5% of the powder is commercial sodium dichromate which acts as a solution activator and a metal depolarizer, thus facilitating the electrochemical deposition of the phosphate coating. The Banox solution is not heated, but agitated pneumatically. It is claimed that it is as effective as other compounds, is easier to handle, costs 60% less for replacement from consumption, and requires no heating equipment.—J. C. R.

Characteristics of Greases as Related to Antifriction Bearing Applications. E. S. Carmichael and R. C. Robinson. (Mechanical Engineering, 1950, vol. 72, Feb., pp. 137–141, 143, 144). The following characteristics of greases for antifriction bearings are discussed : Consistency, apparent viscosity, structural stability at elevated temperatures, resistance against separation of oil, chemical stability, water-resistance and rust-preventative properties, and film strength.—R. A. R.

WELDING AND FLAME-CUTTING

Square Tubes in Welded Construction. G. Coll. (Boletin de Informacion del Instituto de la Soldadura, 1949, No. 2, pp. 41–43). [In Spanish]. The author explains why the square tube is the section most suited to the conditions of tensile, compression, and bending. There are two commercial types of square tubes in Spain : 50 × 50 × 4 and 25 × 25 × 3 mm. Some typical constructions are described wherein these have been used.—R. S.

Stress-Relief of Welded Structures. R. Weck. (Revue de la Soudure/Lastijdschrift, 1949, vol. 5, No. 3, pp. 127–136). Annealing at between 600–651° C. relieves the stresses in the metal, makes it more ductile and prevents temper- and hydrogen-embrittlement. The annealing for welded structures is only required if there is a danger of corrosion or if the metal is susceptible to fracture due to the service or manufacturing temperatures. It should be used for structures made from high-carbon (more than 0·2%) or alloy steels. The causes of fractures occurring during or immediately after manufacture are discussed.—R. F. F.

The Resistance and Calculation of Welded Structures Made in Steel A52. L. J. Vandeperre and A. Sariban. (Revue de la Soudure/Lastijdschrift, 1949, vol. 5, No. 2, pp. 66–86; No. 3, pp. 148–172; No. 4, pp. 213–228). The objects of the tests described were to study the behaviour of welded structures made in steel A52 under various stresses and to formulate calculations for maximum permissible stresses. A comparison of the results with those of previous tests on steel 37 is made, and the application of the calculations to steels 45 and H.56 is discussed.—R. F. F.

Welding of Rails and the Fatigue Resistance of Welded Joints. M. P. Hustin and W. Soete. (Revue de la Soudure/Lastijdschrift, 1949, vol. 5, No. 2, pp. 87–105). The different methods of welding used for tramway rails and their effect on the fatigue-resistance of the welded joints is described. The methods used for welding the rails tested include thermit, arc, resistance, and oxy-acetylene welding. Fatigue tests of an unwelded rail are provided for comparison.—R. F. F.

Welding Cuts Costs in Deep Drawing Front Fenders. A. B. Mooers. (Iron Age, 1950, vol. 165, Jan. 26, pp. 73–76). A deep and complicated motor-car wing, difficult to draw from a flat sheet is made in the following manner: A deep **V** is cut from one end of a specially shaped sheet and, by folding, its edges are brought together; they are then welded with a helium shielded arc and a low-alloy filler-rod. The shape so produced is drawn, perforated, and trimmed; the weld resists this deformation very well.—J. P. S.

New Melting Shop at Abbey Works for the Steel Company of Wales, Ltd. J. Warley. (Welder, 1949, vol. 18, July–Sept., pp. 51–54). The new melting shop being erected at the Abbey Works, Margam, is 1870 ft. long and 398 ft. wide, of entirely welded construction. The design requires a number of 110-ft. span (by 12 ft. deep) girders weighing 100 tons each; these, like other parts of the steel work, have been made in a specially equipped fabrication shop, which will later be used as a mould preparation shop.—J. P. S.

The Structural Metalwork of the New Shop Housing the Sheet Mills of the S.A. d'Espérance-Longdoz (Liège). F. Hébrant. (Ossature Métallique, 1950, vol. 15, Jan., pp. 7–12). An illustrated description is presented of the welded structural work of buildings housing the sheet mills of the S.A. d'Espérance-Longdoz at Liège.—J. C. R.

Rolling Mill Shops in Structural Metalwork. (Ossature Métallique, 1950, vol. 15, Jan., pp. 13–17). An illustrated description is presented of the welded structural work of the building housing the new sheet rolling mills of the Société Arbed at its Dudelange (Luxemburg) works.—J. C. R.

The New Buildings of the Société Ferblatil at Tilleur. (Ossature Métallique, 1950, vol. 15, Jan., pp. 18–20). A short illustrated description is given of the welded steel buildings housing the sheet mills of the Société Ferblatil (a subsidiary of the Société Cockerill) at Tilleur.—J. C. R.

New Strip Buildings of the S.A. Phenix Works. (Ossature Métallique, 1950, vol. 15, Jan., pp. 21–22). An illustrated description is presented of the welded steel buildings constructed to house the strip mills and continuous pickling plant of the S.A. Phenix Works.—J. C. R.

How to Repair Tools by Atomic Hydrogen Welding. R. J. Tierney. (Iron Age, 1950, vol. 165, Apr. 13, pp. 86–88). Atomic hydrogen arc welding may be used to salvage tools and dies by the application of filler metal to cracks and flaws, and of hard-facing metal to worn edges. A special advantage of the process is that the intense heat of the arc enables heating to be localized.—J. P. S.

The Qualification of Welders. J. Biernacki. (Przeglad Techniczny, 1948, vol. 69, May 15, pp. 178–183; June 1, pp. 202–206). [In Polish]. Methods of testing the qualifications of welders for different types of work are suggested and discussed.—W. J. W.

The Deseaming Blowpipe. Its Use in the Manufacture of Special Steels. C. Marizy. (Société Française de Métallurgie, Oct. 6, 1949: Revue de Métallurgie, Mémoires, 1950, vol. 47, May, pp. 395–398). The author discusses the use of the oxy-acetylene blowpipe for deseaming ingots of special steels, the mode of operation, gas consumption, the cost, etc.—A. E. C.

Preparation of Metals for Brazing and Welding. J. G. Newell. (New Zealand Engineering, 1949, vol. 4, Sept. 15. pp. 789–790: Australasian Engineer, 1949, Dec. 7, pp. 45–46). The importance of cleanliness in welding operations is stressed in this short paper, and recommendations are also made on the reduction of distortion.—R. A. R.

Gaseous Fluxes for Brazing Steel. A. P. Edson, D. G. Paquette, and I. L. Newell. (Journal of Metals, 1949, vol. 1, Sept., pp. 25–27). The authors discuss the advantages of the use of gaseous fluxes for the brazing of steel, with special reference to boron trifluoride which is said to be particularly effective. Tests of this material showed that the wetting and flow of molten brazing alloys were superior to that normally exhibited by conventional fluxes. No evidence of the contamination of the steel surfaces was found.—R. E.

Powder Cutting [Coupage Oxy-cinétique]. A. E. Leduc. (Ossature Métallique, 1950, vol. 15, Jan., pp. 37–41). A detailed illustrated description is presented of 'oxy-kinetic' cutting, in which small particles are introduced into the oxygen stream and drive out the slag globules during cutting by mechanical action. The particles must resist shock, must not frit, and must be regular in size and free from dust. Results obtained with stainless steels and cast irons are discussed. Thicknesses up to 200 mm. were cut, though this is not suggested as the limit.—J. C. R.

Oxy-Acetylene and Oxy-Hydrogen Cutting. G. Ancion. Revue de la Soudure/Lastijdschrift, 1949, vol. 5, No. 3, pp. 137–147). The principles and application of flame-cutting are described.—R. F. F.

MACHINING AND MACHINABILITY

Influence of the Form of the Raw Material on the Planning of Mechanical Work. M. Rembowski. (Ingenieria e Industria, 1949, Nov., pp. 78–81). [In Spanish]. The planning of machining operations depends on the form of the raw materials. The various types of raw material are classified into rolled bars, forgings, sand castings, and chilled castings. Appropriate methods of machining and the effect of the shape of the piece on machining operations are discussed.—R. S.

Chemico-Mechanical Grinding of Hard Metal Tips. R. M. Kolker. (Stanki i Instrument, 1949, vol. 20, No. 5, pp. 17–19: Metallurgia, 1950, vol. 41, Jan., pp. 133–134). In preparing a hard metal tip for brazing to the steel shank of a lathe tool, the bottom surface must be ground flat to ensure a uniform joint. An apparatus is described by which cobalt-base hard metal tips can be ground in a solution of copper sulphate.—R. A. R.

Novel Repair Saves High Replacement Cost. (Iron Age, 1950, vol. 165, Mar. 9, pp. 70–72). A repair undertaken at the Kaiser Fontana plant is described. A break occurred in one of the jaws of a blooming-mill spade coupling, completely severing the jaw: by the use of cutting torches, the jaws were cut off at right angles to the axis, and a cylindrical surface prepared for the shrinking on of a new cast steel jaw unit. During the cutting, the spindle, which had been preheated, was rotated on a positioner while the torch remained stationary. Compared with an earlier repair in which a hand torch had been used, the amount of metal still to be removed by machining was much reduced.—J. P. S.

Hot Spot Machining Found to Have No Ill Effects on Finished Part Metallurgy. L. T. Friedman. (Iron Age, 1950, vol. 165, Feb. 9, pp. 71–76). Further experiments on hot-machining (*see* Journ. I. and S.I., 1950, vol. 164, Jan., p. 110) have been carried out, in which the effects of turning 3-in. bars of a steel (0·41% C, 0·81% Mn, 0·20% Cr and 3·39% Ni) heated by induction to temperatures of 600–700° F. (310–370° C.), 1000° F. (540° C.), and 1450° F. (790° C.) were studied. Examination of the microstructure, microhardness measurements across a section, and study of the surface by direct analysis and replica techniques have shown that there are no detrimental effects.—J. P. S.

Measuring Machineability on a Constant Pressure Lathe. (Iron Age, 1950, vol. 165, Jan. 19, pp. 68–69). A description is given of the constant-pressure lathe modified from a standard model by the Monarch Machine Tool Co., to be suitable for the constant-pressure lathe test evolved by F. W. Boulger, H. L. Shaw, and H. E. Johnson (*see* Journ. I. and S.I., 1950, vol. 164, Jan., p. 110).

Double Microscope for the Determination of Surface Profiles. E. S. Berkovich. (Zavodskaya Laboratoriya, 1949, vol. 15, Dec., pp. 1490–1491). [In Russian]. Two microscopes arranged at 90° to each other, and an illuminated slit of variable width, are the basis of the instrument described as suitable both for the study of surface profiles and as an accurate, non-contact indicator for the measurement of small displacements. The range of surface roughness dealt with

by the instrument is 10–1000 μ, and it can be used either with a special stand or attached to a lathe. Photographic recording of surface profiles can be made by a simple modification of the instrument. Some examples of such photographs are given.—S. K.

Surface Finishing Stainless Steel. L. F. Spencer. (Iron Age, 1950, vol. 165, Mar. 9, pp. 73–77 ; Mar. 16, pp. 82–85). In the first part of this article, the author describes the grinding of stainless steel with hand grinders and on universal and centreless grinding machines. The second part, dealing with surface finishing, covers the buffing and polishing of these materials.—J. P. S.

CLEANING AND PICKLING

Cleaning Forgings—New Method Cleans Miscellaneous Forgings Cheaper than Pickling, Tumbling and Sandblasting. L. J. Wieschhaus. (Metal Progress, 1949, vol. 56, Oct., pp. 496–497). A brief note is given on economies effected by using airless abrasive blasting for cleaning forgings instead of pickling supplemented by tumbling and sand-blasting.

J. C. R.

Efficient Heating of Descaling Baths. G. Keir. (Metal Progress, 1949, vol. 56, Oct., pp. 516–518). In connection with the gas-fired immersion heating of sodium hydride descaling baths and other molten salt baths, an illustrated account is presented of the use of recirculating heaters with an accurately proportioned air-gas mixture. It is claimed that this method offers superior performance and marked economy over other heating methods, except where electric power is very cheap.—J. C. R.

Satin Finishing Stainless Products. F. Littlejohn. (Steel, 1949, vol. 125, Oct. 17, pp. 81–82). The treatment of stainless steel, both in strip form and as finished components, to obtain a satin finish, is described. Abrasive wheels, belts, and papers are employed.—J. P. S.

From Finishing to Superfinishing. A. Serrado. (Métallurgie, 1949, vol. 81, Nov., pp. 37, 39, 41, 43, 45 ; Dec., pp. 27, 29, 31, 33, 35, 37). The superfinishing of metal surfaces is discussed under the following headings : The Beilby layer ; abrasives used for mechanical polishing ; electrolytic polishing ; machines used for mechanical polishing ; the theory of the roughness of surfaces ; various optical methods for controlling roughness ; and profilometers for measuring the smoothness of polished surfaces.—J. C. R.

A Modern Application of 'Electroforming.' F. Noguer Nadal. (Acero y Energia, 1949, vol. 6, Sept.–Oct., p. 35). [In Spanish]. A new process in the manufacture of abrasive material consists in enveloping the abrasive particles with electrolytically deposited metal. Various patents have been applied for abroad for producing 'diamondized' discs in the following manner : Industrial diamond particles are placed on a circular, flat surface of graphitized wax. A layer of copper, about 0·075 mm. thick is deposited on this, followed by a deposit of nickel on the copper. The nickel deposit is thicker than the layer of diamond particles and covers them completely.

The whole piece is heated to melt away the wax and make the copper dissolve in the nickel in which the diamonds are embedded. The composite layer is fixed with an adhesive to a backing disc.

The advantages of this method are that the diamond particles are oriented so that the maximum cutting power per unit of weight is attained, and so that all the particles are located in the abrasive surface of the disc and are not dispersed in the interior of the mass.—R.S.

PROTECTIVE COATINGS

The Chromium-Plating Plant. Loiseau. (Chrome Dur, 1949, pp. 56–60). This is a general discussion of the chromium-plating process, and the plant required.—A. E. C.

The Chromium Plating of Gauges. Meynier. (Chrome Dur, 1949, pp. 32–36).

The Present Progress of Hard Chromium Plating. P. Morisset. (Revue Générale de Mécanique, 1949, vol. 33, Nov., pp. 459–465). The modern developments in the technique of hard chromium plating are reviewed. The bibliography contains 25 references.—R. F. F.

Application of Electrolytic Polishing and of X-Rays to the Study of Hard Chromium. Preliminary Results on the Influence of the Surface Condition of the Steel Base. P. A. Jacquet and Adrienne R. Weill. (Chrome Dur, 1949, pp. 4–19). Following short notes on the electrolytic polishing of the chromium plating examined and of its surface structure, an account is given of an investigation of the influence of the characteristics of the surface condition of the steel base on the microstructure of thick chromium plating and on the X-ray patterns produced by the coating. The effects observed are discussed.—A. E. C.

Some Applications of Chromium Plating in an Automobile Factory. De Vaulchier. (Chrome Dur, 1949, pp. 48–55). The use of chromium plating for the building up of worn surfaces in motor cylinders and for various purposes in the tool room is briefly discussed.—A. E. C.

The Magnetic Checking of the Thickness of Chromium Plating. Brachet. (Chrome Dur, 1949, pp. 28–31). The principles of methods of estimating chromium coating thicknesses on magnetic basis metals are briefly described.—A. E. C.

Batch Production of Bright Nickel and Chrome Plating. R. Wall. (Journal of the Electrodepositors' Technical Society, 1950, vol. 25, pp. 23–38). The author describes the workshop experiences, production methods, costs, and results obtained by a company which is bright nickel plating parts of its own products. The company is obtaining very efficient and economical results from the process, using a nickel–cobalt (Weisberg) type of solution.—R. A. R.

POWDER METALLURGY

A Phenomenological Theory of Sintering. J. K. Mackenzie and R. Shuttleworth. (Proceedings of the Physical Society, Section B, 1949, vol. 62, Dec. 1, pp. 833–852). The paper deals with the rapid increase of density during the sintering of single substances. The increase of density cannot be explained by volume diffusion of vacant lattice sites or surface migration of atoms, but must involve macroscopic flow. The driving force for this flow is surface tension, and an equation connecting the rate of shear strain with the shear stress defines the resistance to deformation. The density of a compact is calculated as a function of the time for two different laws of deformation, (*a*) that for a solid with a Newtonian viscosity, and (*b*) that for a Bingham solid. The theory predicts that densification is uniform throughout a compact, independent of its shape and size, and suggests that gas pressures of a few atmospheres applied to the outside of a compact may appreciably increase the rate of sintering. Whilst a viscous model may explain the sintering of glasses, it cannot explain that of metals. The experimental data can be explained by a model showing a yield point : on such a model the interaction of one pore with its neighbours is vital, so that pores in powder compacts close and isolated pores do not.—R. A. R.

PROPERTIES AND TESTS

Notes on the Limit of Proportionality, Elastic Limit, and Yield Point of Steel. (Boletin Minero e Industrial, 1949, vol. 28, Nov., pp. 499–500). [In Spanish]. The elastic limit is defined and simple graphs are used to explain its determination. The difficulties in obtaining the limit of proportionality are briefly explained.—R. S.

Investigation of a Relation between the Deep-Drawing Properties of Metals and Tensile Tests. First Results. C. Arbel. (Société Française de Métallurgie, Oct. 5, 1949 : Revue de Métallurgie, Mémoires, 1950, vol. 47, May, pp. 388–394). Experimenting with five materials, one of which was an 18/8 steel, the author found a relation between the deep-drawing properties and the tensile properties, provided that the latter were represented by the 'modulus of cold-work' ; the latter is the exponent in the equation of the stress-strain curve plotted from the 'rational stress' (the load divided by the reduced area), and the 'rational deformation' (the integral of the instantaneous deformation determined on the minimum cross-section, not the length). The deep-drawing properties were measured in a cupping test.—A. E. C.

On a Deep Drawing Test for Medium and Thick Sheets. E. Herzog. (Société Française de Métallurgie, Oct. 5, 1949 : Revue de Métallurgie, Mémoires, 1950, vol. 47, May, pp. 399–408). A new deep-drawing test machine of the cupping type, capable of dealing with metal from 3 to 12 mm. in thickness is described ; it is used in any convenient form of press capable of applying a load of 50 tons. The advantages of the machine, its operation, and typical results obtained are discussed ; it is claimed to give a better indication of the true deep-drawing properties of the material than other machines.

A. E. C.

Bulge Testing of Sheet Metal. H. Thielsch. (Metal Progress, 1949, vol. 56, July, pp. 86–88). An account is given of the bulge test for determining the bi-axial strength of sheet metal.—J. C. R.

Report of Subcommittee XV on Impact Testing. (Proceedings of the American Society for Testing Materials, 1949, vol. 49, pp. 100–104). The work of this Sub-Committee has been concerned primarily with the adaptation of the pendulum machine to a repeated blow test. A Charpy machine modified for repeated blows is briefly described and some results for cast-iron specimens are reported.—R. A. R.

Resistance of a Gun Steel to Explosive Impact. F. Poboril. (Metal Progress, 1949, vol. 56, July, pp. 58–61). The importance of the speed of loading on the impact strength of steel is discussed. A description is given of tests which show that explosive toughness (measured by the powder charge needed to split a heat-treated test piece) has a linear relationship to the Charpy impact of the same steel when tested at −78° C. The theory that the effect of very high speed of impact loading can be replaced by low temperature of a specimen tested at normal speeds is confirmed.—J. C. R.

Significant Strength of Steels in the Design of Machine Parts. C. Lipson, G. C. Noll, and L. S. Clock. (Product Engineering, 1949, vol. 20, Apr. pp. 142–146; May, pp. 124–128; July, pp. 130–135). "Significant strength" is defined as the maximum external load that the part in its fabricated form can sustain under specified conditions. Methods of arriving at this load are considered, including the use of the modified Goodman diagram. Data on the relations between fatigue and tensile strengths, and between hardness and tensile and fatigue strengths are presented in Part I. The effects of cold-work, surface hardening, and plating on the strength of materials used for machine parts, and the relation between fatigue strength and life expectancy are discussed in Part II. In Part III factors for geometric stress concentration, fatigue stress concentration, and notch sensitivity are evaluated in terms applicable to the determination of design stresses for finite and infinite life.—R. A. R.

Discontinuous Crack Propagation—Further Studies. L. D. Jaffe, E. L. Reed, and H. C. Mann. (Transactions of the American Institute of Mining and Metallurgical Engineers, 1949, vol. 185, pp. 683–687: Journal of Metals, 1949, Oct.). Series of apparently discontinuous microcracks were found adjacent to the path of final brittle failure in fatigue specimens, impact specimens and a failed part, made from steel forgings and castings. The cracks were observed every time they were sought in areas close to a brittle transgranular fracture. It is believed that the microcracks indicate that brittle transgranular fracture of polycrystalline metals does not originate at one point and propagate continuously across the material, but nucleates at numerous related points, leading to a series of microcracks which subsequently link up. Microscopical evidence was also found which is interpreted to mean that final fracture in a fatigue specimen does not occur by propagation inwards, in a brittle fashion, of the progressive 'fatigue crack.' Rather, brittle fracture originates closer to the neutral axis and links, subsequently, with the fatigue crack. Previous work by the authors is reported in Journal of Metals, 1949, vol. 1, Aug., p. 526.—R. E.

Economy in Fatigue Testing. M. G. Corson. (Metal Progress, 1949, vol. 56, Oct., pp. 518–519). The author has developed an equation for determining the fatigue limit of a metal, which he claims to have given consistently accurate results within the experimental uncertainties of the original data.—J. C. R.

The Fatigue of Metals. Its Importance in Aeronautical Construction. R. Cazaud. (Technique et Science Aéronautiques, 1949, No. 3, pp. 147–159). The author discusses fatigue of metals with special reference to aircraft construction. He discusses the effects of shape, stress, temperature and corrosion on fatigue and lists the fatigue limits for a number of steels and two light alloys.—R. F. F.

Report of Sub-Committee on Research. (American Society for Testing Materials, 1949, vol. 49, pp. 523–531). This report is an appendix to the Report of Committee E-9 on Fatigue; it consists of some paragraphs on the following significant features of present-day fatigue testing: (1) The crystalline mechanism of fatigue fracture. (2) Can test results on small specimens be used to predict the fatigue strength of full-size structural or machine parts? (3) Brittleness and the fatigue of metals. (4) Fatigue strength at elevated temperatures. (5) Fatigue under a 'spectrum' of repeated stress patterns. (6) Residual stresses and their importance. (7) Effect of surface condition on fatigue strength. (8) Fatigue testing machines. (9) Short-time fatigue tests.—R. A. R.

The Effects of Temperature and Material Structure on the Fracture Properties of Medium-Carbon Steel. J. Miklowitz. (American Society for Testing Materials, 1949, vol. 49, pp. 602–617). The effects of temperature and structure on the transition from ductile to brittle fracture of medium-carbon silicon-killed and silicon–aluminium-killed steel have been investigated using a 10-ton constant-strain-rate tensile testing machine with an automatic load-elongation recorder. The ductility as represented by the conventional axial strain in the minimum section of the neck at fracture was greatest for spheroidized pearlite structures. Both fine and coarse-grained structures of silicon-killed steel showed the highest strain values at all temperatures. A general increase in strain at fracture occurred with testing temperatures decreasing from −20° to −65° C. for all structures. A change from ambient temperature to −20° C. had little effect.—R. A. R.

Dynamic Creep and Rupture Properties of Temperature-Resistant Materials under Tensile Fatigue Strees. B. J. Lazan. (American Society for Testing Materials, 1949, vol. 49, pp. 757–787). The limitations of static testing and the importance of dynamic creep and rupture properties when designing for high-temperature service are discussed. Newly developed dynamic testing machines and measuring equipment are described, and results of tests on a 22/19/19 chromium–nickel–cobalt steel and a 20/20/44 chromium–nickel–cobalt alloy with small amounts of molybdenum, tungsten and columbium are presented. The increased creep and rupture resistance during some of the dynamic tests is discussed in terms of possible metallurgical changes caused by cyclic stress. The data show the greatly increased ductility caused by superimposing stress cycles on a tensile preload.—R. A. R.

Testing Materials at High Temperature. F. G. Tatnall. (Mechanical Engineering, 1949, vol. 71, Nov., pp. 906–910). An illustrated review is presented of current methods of testing materials at elevated temperatures, including short-time stress-strain tests, stress-rupture tests, creep tests, relaxation tests, and fatigue tests.—J. C. R.

Embrittlement Phenomena when Tempering Heat-Treated Steels with a High Phosphorus Content. E. Houdremont and H. Schrader. (Jernkontorets Annaler, 1949, vol. 133, No. 10, pp. 469–501). [In Swedish]. The influence of increased phosphorus content on the toughness of carbon and chromium–nickel steels, hardened and tempered, has been investigated. Embrittlement phenomena were observed not only in the temperature range of temper-brittleness, but also at considerably lower temperatures down to 15° C. A small decline in impact strength, which occurred in all steels, independent of the alloying element, or phosphorus content, on holding at room temperature or at 100° C. was interpreted as a result of carbide precipitation. This phenomenon must be distinguished from another, more marked, embrittlement, which is displaced to lower temperatures by increased phosphorus contents, and which is ascribed to phosphide precipitation. The well-known decline in toughness with high phosphorus contents is attributed to a rapid embrittlement, since the differences are largely eliminated if the tests are carried out immediately after heat-treatment. Lowering the carbon content did not cause any fundamental change, but only decreased the sensitivity, as neither longer time nor higher temperature was necessary to initiate the embrittlement.—R. A. R.

Quench Cracking Factors. D. W. McDowell. (Iron Age, 1950, vol. 165, Jan. 12, pp. 64–67). Studies of quench-cracking in gun tubes forged from basic electric steel indicate that the likelihood of cracking falls with increased pouring temperature and higher finishing temperature, and rises with increased ingot size. The maximum carbon content for freedom from cracking is 0·35%.—J. P. S.

Magnetic Anisotropy in Cold-Reduced Electrical Sheet Steel. A. E. De Barr. (Proceedings of the Institution of Electrical Engineers, 1949, vol. 96, Part II, Oct. pp. 719–728). The observed anisotropy of oriented polycrystalline silicon–iron sheet is discussed with reference to the results of crystal physics. It is shown that, whilst the material can be regarded as homogeneous, *e.g.*, for elasticity or magnetic torque, good agreement is obtained between theory and experimental results on the oriented sheet. An equivalent model aggregate

is described which simulates very closely the observed properties of the sheet. The application of the domain theory of ferromagnetism to the anisotropy of magnetic properties is discussed, and it is suggested that the problems arising might be explained by considering the actual domain configuration of the material. Experimental results on hysteresis loss, permeability, magnetostriction, etc., for oriented sheet are considered in relation to the domain changes taking place during magnetization. The more complex phenomena occurring during alternating current magnetization are considered in relation to the simpler magnetic properties previously discussed.

The Use of Metals at Low Temperature. S. L. Hoyt. (Metal Progress, 1949, vol. 55, June, pp. 821–826). A discussion is presented on the factors which control the low-temperature behaviour of ferritic steels and other metals. The metallurgical and mechanical factors of low-temperature brittleness are examined. These factors, together with the size and design of the part, affect the choice of steels for low temperature service and their treatment.—J. C. R.

Research on Low-Alloy Steels Suitable for High-Pressure Boilers Operating at Temperatures of 575°–600° C. P. Skulari. (Druhý Pracovní Sjezd Horních a Hutních Inženýrů, 1947, May, pp. 145–149). [In Czech]. Soviet research work on low-alloy heat-resisting steels for boilers is reported in this paper presented at the 1947 Convention of Czech Mining and Metallurgical Engineers. The aim was to find a low-alloy boiler steel for operating temperatures up to 650° C., with good hot and cold working properties which would withstand stresses of 3·4 to 4 kg./sq. mm. at 650° C. and a max. creep of 10^{-7} mm./hr. (1% deformation in 100,000 working hr.). Five different steels of the Crolloy type with additions of vanadium, molybdenum, silicon, and niobium were tested, particular attention being paid to the effect of niobium. It was found that niobium has a favourable influence on the properties of the steel and that the steel ' cm 04 ' (containing chromium, molybdenum, vanadium, and niobium) is most suitable for the purpose, since its stability at 700° C., its creep strength at 500° C., and its weldability are better than those of the other steels tested. It is emphasized that the carbide Nb_4C_3 is face-centred cubic.—E. G.

A New Low-Alloy Steel for High-Temperature Use. G. F. Comstock. (Metal Progress, 1949, vol. 56, July, pp. 67–71). Low-carbon titanium steels with over 0·01% of boron hardened appreciably on quenching or air-cooling from 2100° F. and retained an exceptional degree of hardness after tempering. An account is given of the properties of such steels. Hardness on quenching was Rockwell B-85 and this was increased by a long stay at 1100° F. No graphitization was found after 10,000 hr. at that temperature. Stress-rupture tests indicated a life of 10,000 hr. at 1000° F. and 50,000 lb./sq. in. Boron and titanium (or columbium) additions were also found to improve the stress-rupture properties of 6% chromium steel.—J. C. R.

Electromagnetic Methods of Investigating the Condition of Steel Wire Ropes. V. S. Kravchenko. (Bányászati és Kohászati Lapok, 1949, vol. 4, Oct., pp. 420–424). [In Hungarian]. The Soviet Institute for Mining Research carried out investigations on the use of electromagnetic methods of determination of wear and broken wires in wire ropes. Design principles for A.C. and D.C. instruments are described. The D.C. ' defectoscope ' consists of a coil which induces a magnetic field in the direction of the axis of the rope and a secondary coil which feeds the induced voltage into a filter circuit connected to an amplifier and a recording instrument. To obtain a magnetic field in the rope, the windings are oscillated by a vibrator. The windings are made in two semi-circular halves to enable them to be fitted over any part of the wire rope. In the A.C. ' defectoscope ' the resistance is connected across the secondary winding and the secondary voltage is fed from a bridge circuit, *i.e.*, from the centre point of the secondary winding and a variable point of the resistance, to the measuring circuit. The D.C. instrument is much more sensitive than the A.C. one and it can detect a single broken wire inside the rope. Maximum sensitivity for detecting faults is obtained for a field of about 20,000 Gauss. Impulses of several millivolts are obtained with a rope speed of 1 m./sec. Two types of measuring circuit were developed, one working with a photo-relay-type amplifier and one with an electronic tube amplifier. The reduction in cross section due to wear can be measured with an accuracy of 1% by means of a ballistic galvanometer, but this is only suitable for laboratory work.—R. G.

Graphitic Toolsteel—Substituted for 18-4-1 High Speed Steel in the Manufacture of Arbors. E. C. Wallace. (Metal Progress, 1949, vol. 56, Oct., p. 512). A brief note is presented on the use of graphitic steel in place of high-speed steel arbors for turning, sharpening, and grinding.—J. C. R.

The Probolog, for Inspecting Nonmagnetic Tubing. G. A. Nelson. (Metal Progress, 1949, vol. 56, July, pp. 81–85). An illustrated account is given of the ' Probolog,' which is an instrument which detects and indicates or records all types of irregularities in tubes of non-magnetic metals such as brasses and austenitic steels found in heat exchangers. It reveals the presence of holes, cracks, internal or external corrosion, pitting, recrystallization, and non-uniformity of wall thickness. The instrument is portable and consists of interchangeable probes of diameters to fit standard sizes of tubing, a mechanical probe puller synchronized with the chart drive of the recorder, an electronic recorder, and an air gun to project the probe to the far end of the tube.—J. C. R.

Inspecting Forged Turbine Blades and Buckets. R. F. Wagner. (Steel, 1949, vol. 125, Oct. 24, pp. 66–67). At the Cleveland, Ohio, works of the Steel Improvement and Forge Co., very careful inspection is carried out at all stages of the manufacture of forged turbine blades and buckets. Templates for the dies are inspected and checked for contour before use, and the dies themselves checked carefully with height gauges, vernier protractors, and so on. After the blades are forged, the first blade is examined very carefully for dimensional correctness, and further checks are made during the run. Magnaflux and Rockwell hardness tests are also made. Each blade also receives a final inspection against master templates.—J. P. S.

The Influence of Temperature on the Young's Modulus of Gas Turbine Alloys. G. Vidal and P. Lescop. (Revue Générale de Mécanique, 1950, vol. 34, May, pp. 170–172). A method for determining Young's Modulus is described. With this method, designed specially to test alloys subjected to high temperatures, the modulus E is calculated from the density d and the velocity of sound V by the formula $E = V^2 \times d$. The apparatus used is schematically described, and results are given for the effect of temperature on the Young's Modulus of light alloys, ferritic steels, and austenitic refractory alloys.

Contribution to the Study of the Influence of the Microstructure on the Hot Strength of Steel. G. Delbart and M. Ravery. (Société Française de Métallurgie, Oct. 6, 1949: Revue de Métallurgie, Mémoires, 1950, vol. 47, Mar., pp. 215–233). The research described was carried out on a steel containing: Carbon 0·12%, silicon 0·16%, manganese 0·7%, chromium 0·6%, molybdenum 0·65%, phosphorus 0·02%, sulphur 0·01%, aluminium 0·03%, titanium <0·01%. The mechanical properties in the cold state and other characteristics are recorded. A variety of heat-treatments were applied to the material and it was then subjected to creep tests at various temperatures under various loads. The microstructures of the steel are correlated with the rates of creep recorded between the twenty-fifth and thirty-fifht hours of the test. The variation of the ' Veritas ' strenght (that strength which corresponds to a creep extension of 5×10^{-4}% per hr. between the twenty-fifth and thirty-fifth hours) with temperature, and of the creep rate with the load, was studied. As some structures are liable to undergo modification in different ways while held at high temperatures for long periods, a number of similar creep tests were continued for 1000 hr. to confirm that the results obtained in the shorter tests were still applicable. The results of all the tests are discussed in detail.—A. E. C.

Investigations into Corrosion-Resisting Cast Chromium–Nickel Steel with Special Reference to the Sigma Phase. W. Felix and Eisermann. (Sulzer Technical Review, 1949, No. 2, pp. 1–6). Mechanical, microscopical, and magnetic permeability tests have been made on specimens of cast austenitic-ferritic 20/14/4 chromium–nickel–molybdenum steel to determine the influence of heat-treatment on the formation of σ phase. The conclusions were: (1) From room temperature up to about 950° C. the steel in question is in the $\gamma + \sigma$ state. Above 950° C. the σ phase diminishes with rising temperature, while new ferrite is formed. At 1100° to 1150° C. the σ phase has disappeared almost completely. With rising temperature, the steel runs through a two-phase equilibrium $\gamma + \sigma$, a three-phase equilibrium $\gamma + \sigma + \alpha$,

and finally reaches a two-phase region $\gamma + \alpha$; during cooling the process is reversed. (2) With sufficiently rapid cooling from the $\gamma + \alpha$ region, the σ separation can be prevented and the austenitic-ferritic structure cooled to room temperature. The undercooled ferrite is unstable and, upon tempering between 500° and about 950° C. changes into σ phase; this change is a diffusion process. (3) The rate of σ formation in the ferrite is highest in the 800–900° C. range. (4) The σ phase causes a considerable loss of toughness, whilst the hardness is only slightly affected.—R. A. R.

METALLOGRAPHY

Application of the Electron Microscope to the Study of Heat-Resisting Cr–Mo Steels. L. Habraken. (I.R.S.I.A.: Comptes Rendus de Recherches, 1949, No. 1, Nov., pp. 55–70). After describing the methods available for preparing the replicas used under the electron microscope, the author gives the results of his examination of a heat-resisting steel containing 0·1% of carbon, 2–3% of chromium, and 1% of molybdenum. He concludes that the carbides formed during heat-treatment are not necessarily stable at the temperature of creep tests, even though this temperature may be 225° C. below that at which tempering was carried out. In the light of earlier investigations on the ageing of metals and the modification of carbides during tempering, it may be assumed that the complex carbides formed during heat-treatment are later replaced by more simple carbides. Stresses played a part in the formation of carbides; in particular, in parts of the metal submitted to stress and for certain stress values, fresh precipitations were observed which were distinguished by their elongated form and their orientation.—E. A. C.

The Diffusion and Solubility of Carbon in Alpha Iron. J. K. Stanley. (Transactions of the American Institute of Mining and Metallurgical Engineers, 1949, vol. 185, pp. 752–761; Journal of Metals, 1949, Oct.). The Van Orstrand-Dewey and the Grube methods were used to determine the diffusion and solubility of carbon in alpha iron. Both methods gave lines meeting at the same point to give a maximum solubility of 0·019% carbon at 725° C.—R. E.

New Structural Diagrams for Alloy Cast Irons. H. Laplanche. (Metal Progress, 1949, vol. 55, June, pp. 839–841). Two sets of structural diagrams for alloy cast irons are given. Six diagrams show the limiting curves of the pearlitic field for cylindrical test bars 30, 20, and 10 mm. in dia. with nickel contents of 0·5, 1·0, and 1·5%, and with chromium contents of 1 and 2%. A further three diagrams show similar curves for 1 and 2% molybdenum.—J. C. R.

A New Method for Surface Reproduction. K. B. Mather. (Metal Progress, 1949, vol. 56, Aug., pp. 225–227). An investigation has been carried out to study the effect of pressing a reasonably flat metal surface into a fine-grained photographic emulsion at about 15,000 lb./sq. in. It was found that when the plate was developed the surface contours were reproduced. A distinct three-dimensional appearance resulted, the high portions of the surface being responsible for denser regions in the developed emulsion. It is suggested that, if standardized, the method might give a quantitative measure of surface roughness. Also if the technique is improved it might be possible to record grain boundaries on polished or etched metal.—J. C. R.

Determination of Internal Stresses of the Second Type. P. Skulari. (Druhý Dracovní Sjezd Horních a Hutních Inženýrů, 1947, May, pp. 127–144). [In Czech]. The author, in a paper before the 1947 Convention of the Czech Mining and Metallurgical Engineers, classifies internal stresses into three different types: The first type is that inside the individual crystals, the second is that occurring between individual crystals owing to their non-uniform size, and the third is that between individual crystallites. A method is described by which the second type can be determined quantitatively by X-ray diffraction. This method is based on the relation between the width of the interference lines $K\alpha_2\alpha_1$, the change in the Bragg angle, and the change of the lattice constant resulting from internal stresses of the second type. For calculating these stresses the author has modified the Cagliotti-Sachs equation, which defines the relation between the change in lattice constant and the internal stress. It was found that, for low-carbon steels, the optimum annealing conditions were 460° C. for 1 hr. and cooling in air.—E. G.

Preparation of Metal Single Crystals. A. N. Holden. (American Society for Metals, Oct., 1949, Preprint No. 35). Basic processes used to grow or form single crystals of metal are described, together with some variations that have been developed and the experimental difficulties encountered. The degree of imperfection and the causes of imperfection are discussed. Methods of growing crystals of desired orientations are described. A list of 159 references on the preparation of single crystals is appended.—J. C. R.

The Free Energy Change Accompanying the Martensite Transformation in Steels. J. C. Fisher. (Transactions of the American Institute of Mining and Metallurgical Engineers, 1949, vol. 185, Oct., pp. 688–690: Journal of Metals, 1949, Oct.). The author presents the work of other investigators on the influence of temperature and composition on the free energy change accompanying the transformation of austenite to ferrite.—R. E.

Kinetics of the Austenite→Martensite Transformation. J. C. Fisher, J. H. Hollomon, and D. Turnbull. (Transactions of the American Institute of Mining and Metallurgical Engineers, 1949, vol. 185, pp. 691–700: Journal of Metals, 1949, Oct.). The theories of nucleation and growth are applied to the austenite→martensite transformation in steels. Nucleation in single component systems, and in the two-component iron–carbon system are discussed. M_s temperatures and martensite transformation curves are calculated for each of several alloy steels of varying carbon and chromium contents, and are compared with those determined experimentally by Lyman and Troiano (Transactions of the Society for Metals, 1946, vol. 37, p. 402) and Harris and Cohen (Transactions of the American Institute of Mining and Metallurgical Engineers, 1949, vol. 180, p. 447).

Thermodynamics of the Eutectoid Zone in Carbon and Low Alloy Steels. Parts II and III. F. Munoz del Corral. (Instituto del Hierro y del Acero, 1949, vol. 2, Oct.–Dec., pp. 52–66). [In Spanish]. Continuation of a series of articles (*see* Journ. I. and S.I., 1950, vol. 164, Feb., p. 247.

The second part deals with binary and more complex systems. The third part explains the thermodynamics of the transformations in the sub-critical zone, in the upper zone (pearlite and troostite), and the formation of martensite and bainite.—R. S.

The Thermodynamics of Iron Alloys. W. Oelsen. (Iron and Steel Institute, 1950, Translation Series, No. 398). This is an English translation of a paper which appeared in Stahl und Eisen, 1949, vol. 69, July, pp. 468–475 (*see* Journ. I. and S.I., 1950, vol. 164, Mar., p. 379).

CORROSION

Corrosion Resistance of Molybdenum Stainless Steels Deposited during Welding. A. L. Schaeffer and R. D. Thomas, jun. (Revue de la Soudure/Lastijdschrift, 1949, vol. 5, No. 4, pp. 198–212). Eleven samples of stainless steel welds of composition equivalent to American Iron and Steel Institute Nos. 316, 317, 318, and 316e (very low carbon) were tested by boiling in 65% nitric acid and in copper sulphate in solution in sulphuric acid. Each composition was tested immediately after welding and after four different heat-treatments. After testing for 500 hr. in boiling copper-sulphate/sulphuric-acid solution, only the steels containing intergranular carbides showed signs of corrosion, these were steels 316 and 317 with less than 4% ferrite. With boiling nitric acid rapid corrosion was only found with specimens which had been tempered and annealed at 1050° C. As all steels were affected, it was thought that an intergranular precipitation of the sigma phase had taken place. Treatment between 700° and 850° C. reduces the ductility but increases the resistance to nitric acid. Above 850° C. the rate of corrosion increases owing to the carbide and the sigma phase coalescing. No different results were obtained by testing welded joints in nitric acid, these results being similar to those obtained by tests on the weld metal.—R. F. F.

The Use of Corrosion-Resistant Alloy Steels in the Heavy Chemical Industry. F. H. Keating. (Nickel Bulletin, 1949, vol. 22, Dec., pp. 186–190). Four classes of corrosion-resistant alloy steels suitable for use in the heavy chemical industry are discussed: (1) Plain 18/8 chromium–nickel steel; (2) 18/8 chromium–nickel steel stabilized with titanium or columbium, which is resistant to intercrystalline disintegration; (3) 18/8 chromium–nickel steel with molybdenum additions which confer resistance to attack by certain corrosive liquors; and (4) other highly alloyed steels. Deductions from the properties of the material, deductions from previous

experience in similar work, and corrosion testing influence a designer in his choice of steel, and are discussed here in their relation to the application of chromium–nickel austenitic steels.—J. C. R.

Interfacial Molecular Destruction in a Fitted Joint. Chambaud. (Chrome Dur, 1949, pp. 37–39). This is largely a summary of the conclusions drawn by G. A. Tomlinson, P. L. Thorpe, and H. J. Gough in their paper on "An Investigation of the Fretting Corrosion of Closely Fitting Surfaces" (*see* Journ. I. and S.I., 1931, No. I, p. 377A). Nickel-plating is suggested as a remedy for surfaces damaged by fretting corrosion.—A. E. C.

Investigations on the Oxidation of Iron–Nickel Alloys at High Temperatures. J. Bénard and J. Moreau. (Société Française de Métallurgie, Oct. 4, 1949 : Revue de Métallurgie, Mémoires, 1950, vol. 47, Apr., pp. 317–323). The mechanism of the oxidation in air at raised temperatures of pure iron–nickel alloys with 5, 10, 20 and 30% of nickel was investigated. Following a more general description of the appearance of the oxidized specimens a detailed account is given of the mechanism of oxidation on the surface and in the interior of the specimens. In conclusion the kinetics of oxidation are touched on.—A. E. C.

New Notes on the Corrosion of Gas Cylinders. A Pignot. (Chaleur et Industrie, 1949, vol. 30, Oct., pp. 249–254). The corrosion of gas cylinders is considered mainly from the aspect of the contents of the cylinders. Prussic acid when above a certain strength appears to be the chief corrosive agent.—J. C. R.

Prevention of Corrosion by Means other than Protective Coatings. F. L. LaQue. (United Nations Scientific Conference on the Conservation and Utilization of Resources : Corrosion, 1950, vol. 6, Feb., pp. 72–77). *See* Journ. I. and S.I., 1949, vol. 164, Mar., p. 379.

ANALYSIS

Examination of Brown's Method for Determining the Hydrogen Content of Steel. M. Smialowski, E. Wrzesinska, and W. Stoklosa. (Prace Badawcze Glownego Instytutu Metalurgii i Odlewnictwa, 1949, No. 2, pp. 181–182). [In Polish]. W. D. Brown's method (*see* Journ. I. and S.I., 1945, No. I, p. 99A) for the determination of hydrogen in steel has been examined using steel samples containing 0·27% of carbon, 0·59% of chromium, and 3·43% of nickel. The samples were heated in an atmosphere of hydrogen for 1 hr. at 900° C. and quenched. The loss of hydrogen during ageing in the open air at 20° C. is graphically presented.—W. J. W.

Rapid Photometric Determination of Copper in Ferrous Alloys. R. A. Dunleavy, S. E. Wiberley, and J. H. Harley. (Analytical Chemistry, 1950, vol. 22, Jan., pp. 170–172). Copper may be determined in plain and low-alloy steels and cast irons by the following method : A nitric acid solution of the sample is treated with Rochelle salt (potassium sodium tartrate) to form a complex with the iron, and the *p*H is adjusted to 11·3–12·3 with sodium hydroxide. A small quantity of α-benzoinoxime solution is added and the green copper complex so formed is extracted with chloroform. The colour is then measured with a spectrophotometer or filter photometer. Nickel and cobalt interfere with the accuracy of results when present above 0·5% and 0·25% respectively.—J. P. S.

Determination of Aluminium Nitride Nitrogen in Steel. H. F. Beeghly. (Analytical Chemistry, 1949, vol. 21, Dec., pp. 1513–1519). The nitrogen present in a steel as aluminium nitride is determined by dissolving away the iron in an ester-halogen mixture, such as bromine and methyl acetate ; in such solutions the aluminium nitride does not hydrolyse as it does in contact with water or aqueous solutions. The nitrogen may be determined in the residue by the use of a simple micro-Kjeldall apparatus. It is claimed that the elements usually found in carbon steels do not interfere, and that the determination has already been used on several thousand heats of open-hearth and Bessemer steels.—J. P. S.

Determination of Phosphorus in Iron Ore. J. L. Kassner and Mary A. Ozier. (Analytical Chemistry, 1950, vol. 22, Jan., pp. 194–195). The time required to determine phosphorus in iron ore is shortened not only by using a double-strength citrate-molybdate solution, but by separating the ammonium phosphomolybdate at the boiling point. Free molybdic acid does not separate at this temperature and the alkalimetric titration may be carried out in normal manner.

Estimation of Free Quartz in Lorraine Iron Ores. J. Aubry and G. Turpin. (Société Française de Métallurgie, Oct. 6, 1949 : Revue de Métallurgie, Mémoires, 1950, vol. 47, Feb., pp. 146–147). The ore is first treated with a buffer solution of acetic acid and sodium acetate of *p*H 2·5 to remove carbonates of lime and magnesia and some of the siderite (iron carbonate). Then, after filtering and washing, the residue is attacked with boiling 20% solution of $Na_2S.9H_2O$ (*p*H about 12). This peptizes the colloidal and combined silica, but leaves the free silica unaffected ; most of the iron is converted into colloidal iron sulphide. The insoluble residue is treated with a hot mixture of nitric and hydrochloric acids, and the final residue is the free quartz of the ore.—A. E. C.

Determination of Sulphates in Nickel Plating Solutions. V. F. Toropova, E. A. Zimkin, and A. A. Popel. (Electroplating, 1949, vol. 3, Dec., pp. 132–133). This is an English summary of the paper which appeared in Zavodskaya Laboratoriya, 1949, vol. 15, pp. 404–407. (See Journ. I. and S.I., 1949, vol. 163, Nov., p. 366).

A Rapid Method of Determining Sulphuric Acid in Chromium Plating Electrolytes. V. A. Il'in. (Electroplating, 1949, vol. 3, Dec., pp. 130–131). This is a translation into English of an article which appeared in Zavodskaya Laboratoriya, 1948, vol. 14, Nov., pp. 1389–1390. The determination of sulphuric acid in chromium plating electrolytes at the Krasnogvardeets Works is based on the electrochemical processes that take place during the electrolysis of the chromium plating electrolyte. A description of the method which takes only 10–15 min., is given. The maximum error is 13% and as this is compensated by the rapidity of determination, the method can be applied in practice.—J. C. R.

A Simple Apparatus for Direct Recording in Spectrum Analysis. K. G. Bylund and H. Rudberg. (Jernkontorets Annaler, 1949, vol. 133, No. 11, pp. 507–518). [In Swedish]. A brief description is given of a direct-reading instrument for spectrochemical analysis, constructed at the laboratory of AB. Järnförädling, Hälleforsnäs, Sweden. The method of using it and some results obtained in routine analysis are given.—R. A. R.

Spectrographic Analysis of Metallic Alloys. M. Scalise. (Metallurgia Italiana, 1950, vol. 42, Feb., pp. 49–52). The author discusses the use of spectrographic analysis in Italian metallurgical laboratories and the factors which have hindered its development. He describes the work carried out in the spectrographic laboratory of a large engineering works.—R. F. F.

Application of Salicylaldoxime to the Spectrophotometric Determination of Iron in Ores. J. P. Mehlig and Dorothy Durst. (Chemist Analyst, 1949, vol. 38, Dec., pp. 76–79). A spectrophotometric method has been developed for the determination of iron in ores ; it depends upon forming a soluble, orange-red complex of ferric iron with salicylaldoxime and measuring the transmittancy at 480 mμ of the resulting colour system.—R. A. R.

Application of Direct Analysis to the Estimation of Steels and Spelters. A. Hans. (I.R.S.I.A. Comptes Rendus de Recherches, 1949, No. 1, Nov., pp. 77–95). A brief description is given of a grating spectrograph in which electron multipliers are placed in one of the orders and a camera in the other ; by this means direct analyses or graphical analyses can be carried out separately or simultaneously. The results obtained in the determination of manganese, silicon, chromium, and phosphorus in steels and of lead and iron in spelter are presented and the factors influencing their accuracy are discussed.—A. E. C.

Analysis of Residual Elements in Steel by Means of a Direct-Current Intermittent Arc. V. Mathien. (I.R.S.I.A. Comptes Rendus de Recherches, 1949, No. 1, Nov., pp. 71–75). The author discusses the light source, the taking of samples and preparation of the electrodes, and the method of estimating residual elements by spectroscopy.—A. E. C.

Determination of Vanadium in Alloy Steels. [13·5–14·5% Cobalt and 4·5–4·8% Chromium]. R. Ishii and S. Hara. (Bulletin of The Institute of Physical and Chemical Research, vol. 22, No. 2, pp. 170–172). [In Japanese].

On the Determination of Arsenic in Iron and Steel by the Distillation Method. M. Sekino. (Bulletin of The Institute of Physical and Chemical Research, vol. 22, No. 9, pp. 864–867). [In Japanese].

Note on Donaldson's Method for Determining Combined Carbon in Malleable Iron. H. A. Schwartz and G. M. Guiler. (American Foundryman, 1949, vol. 16, Sept., p. 53). The authors have found difficulty in getting accurate results when determining combined carbon in malleable iron using Donaldson's method (*see* Journ. I. and S.I., 1943, No. I, p. 228A). Loss of graphite occurred after the addition of ammonium persulphate, and a procedure is described for removing the graphite before the addition of the persulphate. R. A. R.

On the Determination of the Zirconium Present in the Elementary and Combined State in Commercial Metallic Zirconium and Ferrozirconium. I. Wada and R. Ishii. (Bulletin of The Institute of Physical and Chemical Research, vol. 22, No. 1, pp. 112–114). [In Japanese].

Spectrochemical Analysis of Steels, Cast Irons and Zinc. A. Hannick and A. Hans. (Société Française de Métallurgie, Oct. 20, 1948 : Revue de Métallurgie, Mémoires, 1950, vol. 47, Feb, pp. 134–138). Spectrographic methods employed and results obtained by the Centre National de Recherches Métallurgiques, Belgium, in the analysis of steels, cast irons, and zinc are described.—A. E. C.

A Study of the Effect of the Discharge Energy of a Source on the Emission of Spectrum Lines. G. Brucelle. (Groupement pour l'Avancement des Methodes d'Analyse Spectrographique des Produits Métallurgiques, 11th Congress, Jan., 1949, pp. 29–40). [In French]. Spectra obtained from a controlled spark source with rotatry interrupter (Feussner and Durr types) are studied, with special reference to the analysis of steel. The relative intensity of certain pairs of lines, arc/arc, arc/spark, and spark/spark are considered in detail when the energy input is altered by changing the capacity, when the secondary voltage is changed, and when the self-inductance of the circuit is changed. In nearly every case the relative intensity changes are as would have been foreseen from theory; similar tests for duralumin and Mazak are also tabulated. E. van S.

Direct and Graphic Spectrum Analysis by the Same Instrument. P. Coheur and A. Hans. (Groupement pour l'Avancement des Méthodes d'Analyse Spectrographique des Produits Métallurgiques, 11th Congress, Jan., 1949, pp. 45–50). [In French]. An American grating spectrograph is modified to give ultra-violet spectra on a camera in the second order, and on electronic photo-multiplier cells in the first order. The photocell currents are used to charge very stable condensers, and these charges are measured (after about 20–30 sec. exposure) by a high-impedance amplifier and integrating circuit with a pen recorder. Circuit details are not given, but typical statistics of replicate analyses of alloy steels give coefficients of variation of 0·6 to 0·8% for direct and 1·6% for photographic results from the same samples. The source used was an ARL Multisource unit.—E. van S.

Application of the Line-Breadth Photometric Method to the Analysis of Zinc, Steel and Cast Iron. A. Hans. (Groupement pour l'Avancement des Méthodes d'Analyse Spectrographique des Produits Métallurgiques, 11th Congress, Jan., 1949, pp. 51–55). [In French]. Using a controlled arc from an ARL Multisource unit, spectra are recorded on a grating spectrograph from the arc between a metal surface and a graphite point. As well as measuring line intensities, the widths of selected iron lines are measured at a density level corresponding to the peak density of a line of the minor constituent. These widths, read from the microphotometer traverse screw, are plotted against composition to give a calibration line which is undisturbed by variations in the photographic process. For manganese, copper, tin, and boron in steel the line-breadth method is more precise than the method based on line-density comparisons ; for silicon, nickel, and chromium the contrary holds. For cast iron the line-breadth method is more precise for manganese, and similar to the density method for silicon. In general, the advantage of the new method is greatest when very faint lines must be measured, as for tin and boron, since the calibration lines, instead of being straight, are curved so as to give greater precision at low concentrations.—E. van S.

Evaluation of Spectrograms of High Speed Steels for Minor Elements. Plate Calibration Method. B. N. Bhaduri. (Indian Journal of Physics, 1949, vol. 23, Aug., pp. 347–362). The method of plate calibration developed by D. M. Smith for evaluating spectrograms of non-ferrous metals has been applied for the determination of manganese, silicon, and vanadium (total content 2% max.) in tungsten high-speed steels. The spectra are evaluated and compared by the usual method of plotting the log ratio of the galvanometer deflections.—R. A. R.

An Instrument for Routine Polarographic Analysis. C. H. R. Gentry and D. Newson. (Metallurgia, 1949, vol. 41, Dec., pp. 107–111). In making routine polarographic analyses in the works laboratory, the recording of the complete polarogram and the graphical construction to obtain the diffusion current are to be regarded as time-wasting operations. The authors describe a first attempt at the design of an instrument for measuring the diffusion current directly, intended specifically for routine metallurgical analysis. R. A. R.

On the Relation Between the Potential and Current Density in an Active Electrode. A. Rius and S. Polo. (Anales de Fisica y Química, 1949, vol. 45B, Nov., pp. 1323–1332). [In Spanish]. In the discharge of hydrogen ions on a mercury cathode, the constant b of Tafel's equation

$$E = a + b \times \log i$$

is found to be about 0·116 V., provided that the surface of the electrode is homogeneous. With the polarograph, the value of b is only about three-quarters of the corresponding value with the static mercury electrode. The effect of diffusion is considered and the results obtained with a dropping mercury electrode are given.—R. S.

Nephelometric Test. G. Petracchi. (Metallurgia Italiana, 1950, vol. 42, Feb., pp. 58–59. The author studied the phenomenon of liquids becoming turbid when ferrous materials are immersed in them. He shows how the course of this process can be approximately determined by analysis, also that the resistance of ferrous metals to corrosion can be determined by this means, even when the metals have been subjected to protective treatment. These tests can also establish the degree of resistance to corrosion of ferrous metals in relation to their internal energy due to magnetization on mechanical stressing.—R. F. F.

HISTORICAL

Sidney Gilchrist Thomas. Sir Charles Goodeve. (Engineering, 1950, vol. 169, Apr. 14, pp. 420–422). An account is given of the life of Sidney Gilchrist Thomas (born April 16, 1850, died February 1, 1886) inventor of basic linings for the Bessemer converter which enabled phosphoric iron to be blown and made into steel, leaving the phosphorus in the slag.—R. A. R.

History of the Manufacture of Tinplate. L. Barreiro. (Boletin Minero e Industrial, 1949, vol. 28, Oct., pp. 437–438). [In Spanish]. Manufacture of tinplate commenced about 1600 in Central Europe. An Englishman, Andrew Yarranton, studied the process in Bohemia, and brought back plans to England for producing tinplate in Wales, based on local tin and the ores of the Forest of Dean and Irish charcoal. His plans did not succeed, and it was not till 1720 that John Hanbury started up a plant at Pontypool. Spain began the production of tinplate in 1892 at the La Iberia works now belonging to the Altos Hornos de Vizcaya.—R. S.

The Iron and Steel Industry of the El Bierzo Region in the XVIIIth Century. S. Gomez Nunez. (Boletin Minero e Industrial, 1949, vol. 28, Dec., pp. 561–566). [In Spanish]. This is a historical survey of the industry. Local ores are described. The establishment of a Royal Iron Factory in 1805 for making arms from the iron ore of Formigueiros, and the conversion of the Catalan forge to a practical blast-furnace are described. The impact of the Peninsula War on the industry is explained.

The personality of the Spanish general Munarriz, who combined the virtues of technical knowledge and of military skill, is dwelt on.—R. S.

ECONOMICS AND STATISTICS

Scrap—Metallurgical Problem of Europe. L. Barreiro. (Boletin Minero e Industrial, 1949, vol. 28, Dec., pp. 553–560). [In Spanish]. An attempt is made to analyse the scrap situation in Europe. The types and proportions of scrap, and the imports and exports of foreign countries before and after the war are compared. The factors affecting favourably and adversely the scrap situation in 1949 are given and an estimate of consumption and production of scrap in Europe in 1951 is made. Conditions for European self-sufficiency in scrap in 1951 are stated. Figures are given to illustrate the changes

in the proportion of pig iron used in steelmaking and in foundries in the main steelmaking countries. The scrap situation in France and Italy is dealt with in more detail.

Finally, there is a useful diagram of scrap production and consumption in Europe for 1936 to 1938 with the estimated figures for 1951.—R. S.

Organization of the Metallurgical Industry in the U.S.S.R. E. Fryczkowski. (Hutnik, 1949, vol. 16, Sept.–Oct., pp. 377–382). [In Polish]. Plans are presented showing the structure of the organization of the metallurgical industries of the U.S.S.R., and the structure is explained.—R. A. R.

MISCELLANEOUS

Lighting in Iron and Steel Works. G. W. Levey. (Journal of The Iron and Steel Institute, 1950, vol. 165, May, pp. 91–96). The subject of lighting in iron and steel works is examined from a number of aspects and it is asserted that inadequate lighting is usually due to lack of appreciation of a number of important factors, particularly lighting intensity, which are reviewed in the paper. The intensities suggested for various applications are high compared with those in use in some older works, but are justified by increased quantity and quality of output. Lamps and fittings, switching, current supplies, and distribution have a great bearing on efficiency, reliability, and cost, and should be selected to suit each particular application. The amount of work done in the open in iron and steel works and the heavy outdoor traffic of vehicles and operatives justify close attention to exterior lighting. For marshalling yards a few floodlights at high level have advantages over numerous smaller light sources at low level. Road lighting should be good enough to avoid the use of headlights; it has a technique of its own and requires specialized equipment.

Single Objective Safety. D. A. Farrell. (American Institute of Mining and Metallurgical Engineers, 1949, Open Hearth Conference Proceedings, vol. 32, pp. 242–249). A method of analysing the causes of accidents in steelworks and applying efficient methods of prevention is explained.—R. A. R.

Training Men at Republic Steel Corporation. J. S. Kopas. (Iron and Steel Engineer, 1949, vol. 26, Nov., pp. 84–85). An outline is given of the system adopted at the Republic Steel Corporation for the training of technical operating staff.—J. C. R.

Training Men at Bethlehem Steel Company. H. C. Houghton. (Iron and Steel Engineer, 1949, vol. 26, Nov., pp. 81–83). A general survey is presented of the system of training men at the works of the Bethlehem Steel Company. The programme is divided into four major groups, *viz.*, apprentice training, college graduate training, learner training, and special or supplementary training.—J. C. R.

Occupational Analysis of the Metallurgical Profession. R. Troiano. (Metal Progress, 1949, vol. 56, Sept., pp. 344–347). This is a report of a survey carried out by an Advisory Committee on Metallurgical Education of the American Society for Metals. Data are obtained from the 916 replies received to a questionnaire issued to 3000 members of that society. The published figures include the numbers and percentages engaged in different categories and classes of work, the income of metallurgists depending on their responsibility, and the distribution of the time taken up by an individual's daily duties.—J. C. R.

Costing and Modern Accounting Methods in the Metal Industries. S. H. Withey. (Metallurgia, 1949, vol. 41, Dec., pp. 73–74, 106; 1950, Jan., pp. 143–146; Feb., pp. 223–226). Systems of checking and control are dealt with in this series of articles. The first part explains methods of dealing with incoming orders. Part II deals with the control of stores and metal stocks, and Part III with the compilation of prime costs.—R. A. R.

Radio-Active Aids to Metallurgical Research. O. Lamm. (Jernkontorets Annaler, 1949, vol. 133, No. 7, pp. 247–252). [In Swedish]. The paper reviews the methods of using radioactive isotopes and outlines metallurgical problems to which they could be applied.—R. A. R.

BOOK NOTICES

GAYNOR, F. "*Pocket Encyclopedia of Atomic Energy.*" 8vo, pp. 204, 34 charts and tables. New York, 1950: Philosophical Library. (Price $7.50)

The purpose of this book is to present a comprehensive collection of brief explanations and definitions of concepts and terms in the field of nuclear physics and atomic energy to the scholar, researcher, teacher, librarian, student, and intelligent layman.

It is arranged alphabetically, having about 2000 entries; each entry (a word or phrase) is then defined or explained in a few lines and followed in many cases by the German translation of the word or phrase. Some tables are provided, *e.g.*, under "Isotope Table," 20 pages are included reprinting the table from "Atomic Medicine," and a reference is given to Seaborg's "Table of Isotopes."

Each element is entered under the symbol and again under the name where many lines are taken up in repeating the information given in the Isotope Table. Additional information is normally limited to the melting or boiling point and specific gravity. Much space is thereby used unnecessarily, resulting in condensation of other definitions.

Before using a book of this type to look up the unknown, one usually looks up the known. For example, a volt is defined as the practical unit of electric potential and explained in terms of ampères and ohms. Ampères are then defined in terms of volts and ohms! An abampère is admittedly defined correctly, but is quoted as 1 abampère = 10 absolute ampères. This loose treatment, combined with mistakes, undermines ónes confidence in looking up the unknown. Research workers new to nuclear physics would probably want explanations of words such as scaler, head amplifier, or probe units, but these are not included.

Other less useful words are included but are inconclusively defined, such as: "Diffraction—the effect exerted on waves by an obstacle introduced in their path."

One of the most useful features of the book is the Isotope Table, but this information is available in standard textbooks, and it is unlikely that many readers would consider this book worth $7.50.—E. W. VOICE.

GILL, E. T. and E. N. SIMONS. "*Modern Welding Technique.*" 8vo, pp. x + 276. Illustrated. London, 1950: Sir Isaac Pitman and Sons, Ltd. (Price 21*s.*)

Readers will be aware that one of the authors of this book has previously co-operated with Dr. Edwin Gregory in the preparation of books on the manufacture, working, and heat-treatment of steel and will recognize the simple clarity with which complicated processes are treated.

The text is divided into several main sections including forge and resistance welding, fusion welding, and materials, and these sections contain descriptions of all the main welding processes and the metals normally encountered. The book aims at being essentially a textbook for the student, who is assumed to have little previous knowledge of welding. In this, the book is highly successful.

Welding experts may, however, be particularly critical of some of the details in the book, as for instance a process referred to as recessing in spot welding, the illustration for which bears no resemblance to any assembly process at present used in industry. A number of illustrations on spot-welding electrodes and applications of spot welding to thin sheet are almost unintelligible to those who have had close connection with this form of resistance welding. Again, the maximum plate thickness which can be spot welded is given as $\frac{1}{2}$ in., whereas in practice, economical and practical considerations limit the maximum plate thickness to $\frac{1}{4}$ in. In helping the student to decide which process might best be used for material of say $\frac{3}{8}$ in. thickness, the table involved might be considered misleading.

An excellent section on gas welding shows how this relatively well-established process can continue to be written about with good effect; so many points which have escaped the notice of previous authors are critically examined and clearly explained.

Rather an important omission is the argon arc welding process, and although a complete chapter is devoted to inert-gas welding, argon arc welding only occupies a few lines of it. It would appear that the authors obtained their information for this chapter from America, because Heliarc welding is the particular process considered and the chapter

gives a great deal of detail, including the type of container required for helium storage. The value of this information is particularly small in this country, since helium is not commercially available as it is in America. Other American data have been used for reference in writing on the resistance welding of aluminium and its alloys, and unfortunate comparisons are made between British and American practice which are not technically accurate. American formulæ are given for electrode tip sizes, but no reference is made to existing British formulæ.

The chapters on steel and non-ferrous metals give a fair amount of detail on the welding of wrought and cast iron, alloys steels, aluminium and its alloys, stainless steels, and non-ferrous metals. These chapters should be particularly useful to the student because they put him in a position to determine for himself the correct fields of application for welding.

A subject badly neglected so far is literature on the training of welders and safety in welding. There are chapters devoted to both of these subjects and they should be of considerable use to the beginner.—A. J. HIPPERSON.

"*Gmelins Handbuch der anorganischen Chemie.*" 8. Auflage. System-Nummer 8. "*Aluminium.*" Teil A, Lieferung 8. "*Die ternären Legierungssysteme: Aluminium–Eisen–Kohlenstoff, Aluminium–Eisen–Silicium.*" 8vo, pp. 1235–1370. Clausthal-Zellerfeld, 1950: Verlag Chemie G.m.b.H. (Price DM 30.–)

The four previous numbers of the Gmelins Handbook on aluminium have covered the alloys of aluminium with silicon to radium, zinc to uranium, manganese to rhenium, and iron respectively. The present number covers the alloys with iron and carbon (99 pages) and with iron and silicon (37 pages) and is based on the literature to the end of 1948.

The literature on the aluminium–iron–carbon alloys is concerned almost exclusively with the iron-rich alloys, so that it would be proper to deal with it under iron alloys. Nevertheless, it was for various reasons only possible in the Handbooks on the iron alloys to give a superficial review of the Al–Fe–C constitutional diagram. A thorough review of the literature and a critical discussion of these alloys is therefore included in the present work together with investigations of melts consisting of the pure components of this sytem. The aluminium steels, the aluminium-bearing cast irons, the casting properties, the effect of aluminium on the formation of graphite and on the ageing, machinability, and physical properties of the iron-carbon alloys are also all included; the physical properties cover the crystallographic properties density, thermal expansion, specific heat, and thermal conductivity, but not the electrical and magnetic properties as these have been covered under iron–aluminium and iron–aluminium–carbon. Considerable space has also been devoted to the chemical behaviour and the resistance to corrosion.

The quality of the paper, the printing and the reproduction of the diagrams is excellent and fully up to prewar standards.—R. A. R.

HILBERT, B. R. "*Welding—Design and Processes.*" 8vo, pp. 342, Illustrated. London, 1950: Chapman and Hall, Ltd. (Price 36*s.*)

For producing the first comprehensive book on the design of arc-welded structures published in this country, the author can claim credit. For producing a book which is easy to understand, technically accurate, and full of new ideas, he deserves praise.

The object of the book is to enable engineers to design their products in such a way as to facilitate more economic production by the application of welding. The first chapter is devoted to what might be called a refresher course on fundamental engineering principles, so as to eliminate the necessity for cross-reference to other books, and to make his treatment of distortion and residual stresses as clear as possible.

The most striking chapter in the book is that giving examples of welding designs, and this covers mainly spot welding and arc welding. It is doubtful whether any engineers could look through this particular chapter without getting a really good suggestion for improving, or producing at a lower cost, one of his own products. Supporting chapters include data on joint details, weldability of materials and electrodes to be used, heat-treatment of welded assemblies, preparation of materials and drawings, specifications, inspection, testing, and a review of the available welding processes.

The author draws attention to the fact that the range of rolled steel structural sections available can be put to extensive use in welded structures, but that the flange contours of these sections, designed originally for riveted structures, do not lend themselves readily or effectively to welding. As a temporary measure for overcoming this he suggests some excellent simple modifications that can be made by planing sections, where the length involved is not too great.

Very little information of a misleading nature is put forward. The table referring to the maximum permissible stresses in welds has not taken account of the increase in the maximum permissible stress allowed by B.S. 449 (1948). On the other hand, higher stresses are laid down for welding high-tensile structural steel than are permissible at the moment; rightly or wrongly, the maximum permissible stresses in welds and high-tensile structural steel must not exceed that in mild steel, because mild-steel electrodes are normally used.

The application of welding to the fabrication of clad steel for the manufacture of vessels for the chemical industry is increasing, and certain difficulties are present due to dilution at the weld. This subject is dealt with most ably and should be of considerable value to those responsible for the welding of stainless or nickel-clad material.

A most useful table summarizing recommended welding processes for various materials is given, but argon arc welding is completely omitted; this must be a great disappointment to all those using this new process, particularly those concerned with the use of aluminium and stainless steel.

In some of the recommended heat-treatments put forward for the various designs considered, stress-relieving is referred to which, it is stated, should be by normalizing at 875–900° C. The author goes so far as to suggest that a temperature approaching this is necessary for full stress-relieving. This is at variance with the findings of other technicians who have shown that full stress-relieving can be obtained by a treatment not very much in excess of 600° C.

Of great importance in those industries using welding at the present time is the non-destructive examination of welds for defects. The author puts forward various methods for such examination, but the important developments in the ultrasonic testing technique have been almost completely ignored.

The foregoing defects in the book are completely outweighed by the excellence of the other material contained in it, which is very well written and illustrated, and for normal purposes they could almost be disregarded. A selection of British Standard Specifications relating to welding is listed with other useful data, and a comprehensive index will do much to help in establishing Mr. Hilton's work as a leading reference book.—A. J. HIPPERSON.

MACKWORTH, N. "*Researches on the Measurement of Human Performance.*" (Medical Research Council, Special Report Series No. 268). 8vo, pp. 156. London, 1950: H.M. Stationery Office. (Price 4*s.*)

Two series of experiments are described, designed to test the effects on human responses of continued watchfulness for feeble and irregular signals in the one case and of high temperature and humidity in the other. In the first series, subjects were made to watch for irregular movements of the pointers of clock dials, or for synthetic signals on radar displays, or to listen for sounds of durations longer than those of a standard length. From study of the subjects' responses to these stimuli, the chief numerical factor noted being the number of stimuli missed, the following main conclusions emerge: Accuracy deteriorates rapidly after half an hour of the trials, but can be maintained by spells of half an hour on and half an hour off, or by knowledge of the results achieved during the test spell. Distractions such as the expectation of a telephone message reduce accuracy; high atmospheric temperature has the same effect. If the test period is prolonged to two hours, the proportion of missed signals may be two or three times as high in the last hour and a half as during the first half

hour. These conclusions apply in general to both visual and listening tests.

In the second series of tests, described as " environmental stress tests," there were included a visual test with a form of range finder to assess the effect of lachrymatory gases, and an assault course test of considerable muscular difficulty, including passage through arsenical smokes with and without respirators: the factor noted here was the time to complete the course. The section of this series, which is beyond purely military interest, however, is that in which subjects exposed to high atmospheric temperatures performed simple muscular work (such as lifting a weight by means of a pulley, at the rate of 15 ft.lb./sec.), combined physical effort with muscular control by following the erratic movements of one pointer by operating a weighted lever which controlled a second pointer, copied down morse code messages received over headphones, or followed electrical currents from wiring diagrams. Conclusions from this series were that there is a temperature limit above which even acclimatized men cannot work efficiently indoors. It lies between the effective temperatures of 83° F. and 87·5° F., that is, dry-bulb/wet-bulb hydrometer readings of 90/80° F. and 95/85° F. respectively, and this applies to all forms of intensive work, both physical and mental.

While the exact form of these tests agrees more closely with naval and military service conditions than with those normally encountered in civil life, the report should have considerable interest for industrial welfare officers. Many industrial operations require close attention, and vigilance for departures from normality; here, the conclusions from the first series described should be born in mind. Other operations, especially in iron and steel works, necessitate exposure to high atmospheric temperatures though not in this country to tropical humidity; the maximum temperatures endurable for continued efficiency should be noted by designers of melting- and heat-treatment shops. The comfort of workpeople is shown, by this report, to be an essential part of industrial efficiency.—J. P. S.

NEW PUBLICATIONS

AMERICAN INSTITUTE OF MINING AND METALLURGICAL ENGINEERS. "*Rod and Wire Production Practice.*" (Institute of Metals Division Symposium Series, vol. 3). 8vo, pp. xi + 81. Illustrated. New York, 1949: The Institute.

AMERICAN SOCIETY FOR TESTING MATERIALS. "*A.S.T.M. Specifications for Steel Piping Materials.*" Prepared by A.S.T.M. Committee A-1 on Steel Pipe, Tubes, Castings, Forgings, Bolts. Dec., 1949. 8vo, pp. viii + 320. Philadelphia, 1950: The Society. (Price $3.00)

AMERICAN SOCIETY FOR TESTING MATERIALS. "*A.S.T.M. Specifications for Steel Flat Products.*" Sponsored by A.S.T.M. Committee A-1 on Steel. Steel for Structural Purposes, Steel for Boilers and Pressure Vessels, Corrosion-Resisting Steel, Wrought Iron Plate and Sheet, Metallic Coated Iron and Steel Sheets. March, 1950: 8vo, pp. viii + 311–508. Philadelphia, 1950: The Society. (Price $2.25)

AMERICAN SOCIETY FOR TESTING MATERIALS. "*Manual of Fatigue Testing.*" (Technical Publication No. 91). Pp. 82. Philadelphia: The Society. (Price $2.50 paper, $3.15 cloth)

AMERICAN SOCIETY FOR TESTING MATERIALS. "*Report on the Strength of Wrought Steels at Elevated Temperatures.*" Issued under the Auspices of the A.S.T.M.-A.S.M.E. Joint Committee on Effect of Temperature on the Properties of Metals. Prepared by R. F. Miller and J. J. Heger. Special Technical Publication No. 100. 4to, pp. 109. Philadelphia, 1950: The Society. (Price $3.00)

APRAIZ BARREIRO, J. "*Tratamientos Térmicos de los Aceros.*" Madrid: Escuela Especial de Ingenieros Industriales de Madrid.

BATEMAN, A. M. "*Economic Mineral Deposits.*" 2nd Edition. Pp. 927. New York: John Wiley and Sons, Inc. (Price $7.50)

BLET, G. "*Étude de la Structure des Surfaces.*" (Publications Scientifiques et Techniques du Ministère de l'Air. No. 241). La 8vo, pp. 46. Illustrated. Paris, 1950: Service de Documentation et d'Information Technique de l'Aéronautique. (Price 300 francs)

BRITISH IRON AND STEEL RESEARCH ASSOCIATION. "*The Formulation of Anti-Corrosive Compositions for Ships' Bottoms and Underwater Service on Steel.*" First Report of Joint Technical Panel N/P2. 4to, pp. 26. Illustrated. London, 1950: The Association. (Gratis)

BRITISH IRON AND STEEL RESEARCH ASSOCIATION. "*The Measurement of Surface Finish and its Application to Problems in the Steel Industry.*" By M. R. Hopkins. 8vo, pp. 16. Illustrated. London, 1950: The Association.

BRITISH IRON AND STEEL RESEARCH ASSOCIATION. "*A Summary of the Proceedings of the Conference on The Examination of Metals by Optical Methods.*" Held at Ashorne Hill, Leamington Spa, May 9 and 10, 1949. 4to, pp. 58. London: The Association.

BUSH, G. P. and L. H. HATTERY. "*Scientific Research: Its Administration and Organisation.*" Pp. viii + 190. Washington D.C.: American University Press. (Price $3.25)

CLARK, F. W. "*Tube Works Gauges and Gauging Practice.*" 8vo, pp. 64. Illustrated. Glasgow, Birmingham, and London, 1950: Stewarts and Lloyds, Ltd. (Price 5*s.*)

DAVIES W. "*Foundry Sand Control. Testing, Research and Development.*" 8vo, pp. x + 212. Illustrated. Sheffield, 1950: The United Steel Companies, Ltd. (Price 30*s.*)

DEDERICHS, R. and H. KOSTRON. "*Zwei neue Schnellverfahren zur Kornquerschnittbestimmung.*" F'scap., pp. 31. Illustrated. Weinheim/Bergstrasse. 1950: Verlag Chemie G.m.b.H.

DIETERT, H. W. "*Foundry Core Practice.*" Second Edition, pp. 548. Chicago: American Foundrymen's Society. (Price $10.00)

DINGLE, H. "*Practical Applications of Spectrum Analysis.*" 8vo, pp. 256. Illustrated. London, 1950: Chapman and Hall, Ltd. (Price 40*s.*)

ECKERT, E. R. G. "*Introduction to the Transfer of Heat and Mass.*" Pp. xiii + 284. New York: McGraw-Hill Book Co., Inc. (Price $4)

GAILER, J. W. and E. J. VAUGHAN. "*Protective Coatings for Metals.*" 8vo, pp. xiv + 261. London, 1950: Charles Griffin and Co., Ltd. (Price 24*s.*)

HOFF, H. and T. DAHL. "*Grundlagen des Walzverfahrens.*" (Stahleisen-Bücher, Bd. 9). 8vo, pp. xi + 295. Illustrated. Düsseldorf, 1950: Verlag Stahleisen m.b.H. (Price DM 29.–)

INSTITUTE OF FUEL AND INSTITUTE OF PETROLEUM. "*Modern Applications of Liquid Fuels.*" Report of a Joint Conference. 8vo, pp. viii + 495. Illustrated. London, 1950: Institute of Fuel and Institute of Petroleum. (Price 21*s.*)

LEVASSEUR, A. "*L'Électrochemie et l'Électrométallurgie.*" Seventh Edition. Vol. I. "*Électrolyse.*" (Price 480 francs). Vol. II. "*Fours Électriques.*" Paris: Dunod. (Price 540 francs)

LIPSON, C., G. C. NOLL and L. S. CLOCK. "*Stress and Strength of Manufactured Parts.*" Pp. 259. New York: McGraw Hill Book Co., Inc. (Price $4.50)

LOMMATZSCH, A. "*Kurzer Abriss der Chemie und chemischen Technologie für den Erzbergbau.*" 8vo, pp. 79. Halle (Saale), 1950: C. Marhold. (Price DM 1.70)

MAREK, C. T. "*Fundamentals in the Production and Design of Castings.*" Pp. 383. New York: John Wiley and Sons, Inc. (Price $4)

MICHAUD, R. "*Contribution a l'Étude des Réactions Mutuelles des Cristaux dans la Déformation des Metaux Polycristallins.*" (Publications Scientifiques et Techniques du Ministère de l'Air. No. 240). La 8vo, pp. 98. Illustrated. Paris, 1950. Service de Documentation et d'Information Technique de l'Aéronautique. (Price 500 francs)

NIKURADSE, A. und R. ULBRICH. "*Das Zweistoffsystem Gas-Metall. Physikalisches Verhalten.*" 8vo, pp. 199. Illustrated. Munich, 1950: R. Oldenbourg. (Price DM 16.–)

SMITH, G. V. "*Properties of Metals at Elevated Temperatures.*" Pp. 411. New York; McGraw-Hill Book Co., Inc. (Price $7)

VINCENT, E. T. "*Theory and Design of Gas Turbines and Jet Engines.*" 8vo, pp. ix + 606. London, 1950: McGraw-Hill Publishing Co., Ltd. (Price 64*s.*)

WATTER, M. "*Stainless Steel Structural Design.*" 8vo, pp. 153. Pittsburgh. Republic Press. (Price $5)

IRON AND STEEL
INSTITUTE PAPERS

PLANT DESIGN · MANUFACTURE · RESEARCH · DEVELOPMENT

Ionic Theory of Slag–Metal Equilibria

By P. Herasymenko, Dr.Nat.Sc., and G. E. Speight, B.Sc., F.R.I.C., F.I.M.

Part I—DERIVATION OF THE FUNDAMENTAL RELATIONSHIPS

SYNOPSIS

The equilibrium positions of the principal slag–metal reactions are derived from the laboratory investigations of Chipman, Quarrell, Oelsen, and their co-workers, assuming the ionic structure of slags. The advantage of this theory is shown to be that the number of slag constituents sufficient to describe the physico-chemical behaviour of basic slags is considerably smaller than in the theories assuming the presence of oxide molecules and their compounds.

SULPHUR: The equilibrium $\underline{O} + S'' = O'' + \underline{S}$ does not depend on the content of other constituents of the slag, and can be represented by the equation: $\log k_S^O = \log \frac{[S](O'')}{[O](S'')} = \frac{6500}{T} - 2{\cdot}625$ .....(I)

where k_S^O is the equilibrium ratio and T the absolute temperature.

OXYGEN: The equilibrium connecting the contents of Fe^{++} and O'' ions in slag and the oxygen content of liquid steel is given by: $\underline{Fe} + \underline{O} = Fe^{++} + O''$. The equilibrium ratio $k_O^{Fe} = \frac{(Fe^{++})(O'')}{[O]}$ .....(II)

is found to vary with the ionic fraction of O'' ions according to the equation $k_O^{Fe} = A(O'')^{3/2}$. The dependence of the constant A on temperature is given by the equation: $\log A = \frac{7000}{T} - 3{\cdot}258$. The variation of k_O^{Fe} with O'' content is caused by a change in the activity coefficient of Fe^{++} ions, which is inversely proportional to the $\frac{3}{2}$ power of the O'' content. From these relationships the oxygen content of liquid steel can be calculated from the analysis of basic slag: $[O] = \frac{(Fe^{++})}{A(O'')^{1/2}}$ .....(III)

From equations (I) and (II) the following expression is obtained: $\frac{(S'')}{[S]} = \frac{0{\cdot}043 \times (O'')^{3/2}}{(Fe^{++})}$ .....(IV)

which correlates the desulphurization ratio with the contents of O'' and Fe^{++} in slag.

PHOSPHORUS: The transfer of phosphorus from metal to slag is governed by the reaction: $2\underline{P} + 5\underline{O} + 3O'' = 2PO_4'''$. The equilibrium ratio of this reaction is given by the equation: $k_O^P = \frac{(PO_4''')^2}{[P]^2[O]^{5/2}(O'')^{3/2}}$ ...(V)

Combining equations (V) and (III) gives: $k_{Fe}^P = \frac{(PO_4''')^2}{[P](Fe^{++})^{5/2}(O'')^{1/4}}$ .....(VIa)

Both $\log k_O^P$ and $\log k_{Fe}^P$ are linear functions of the content of Ca^{++} ions.

$$\text{Log } k_{Fe}^P = 7(Ca^{++}) + \frac{14{,}660}{T} - 7{\cdot}44 \text{.....(VIb)}$$

Ca^{++} ions increase the stability of phosphate ions. Fluoride ions strongly increase the phosphorus equilibrium ratios, k_O^P and k_{Fe}^P, and thus favour the dephosphorization of steel.

MANGANESE: The equilibrium ratio $k_{Fe}^{Mn} = \frac{[Mn](Fe^{++})}{(Mn^{++})}$ depends on the content of oxygen and calcium ions in a slag. The dependence on oxygen-ion content is due to variations of the activity coefficient of ferrous ions, so that the activity coefficient of Mn^{++} ions is a function of the calcium content only.

Introduction

Structure of Ionic Melts

Most of the early attempts to derive the slag–metal equilibria were based on two postulates : (i) that the ideal mass action laws are valid for slag–metal equilibria, and (ii) that slags represent liquid solutions of electroneutral oxides and their compounds.

It was mainly the first of these which encouraged previous investigators to undertake the lengthy calculations necessary to derive the various assumed

Manuscript received 15th July, 1949.

Dr. Herasymenko and Mr. Speight are in the Research and Development Department of The United Steel Companies, Ltd., Stocksbridge, Sheffield.

equilibria between ' free ' oxides and their compounds, without any direct evidence for the existence of such compounds. In 1932 Schenck,[1] who developed a most elaborate theory of slag–metal equilibria based on the assumption of ' free ' and combined oxides, discussed the possibility of ionic structure of slags :

> " At present we can hardly avoid neglecting electrolytic dissociation of the slag compounds into their ions. It is certain that the neglect of these phenomena will reduce the theoretical values of the laws represented here,* but there is no clue which would permit a numerical estimate of the error. Unfortunately, we cannot assume complete electrolytic dissociation of the silicates ; in that case it would often be a simple and systematic representation of equilibria, as has been developed, *e.g.*, by Tammann for geo-chemical problems and later, in outline, for steel slag reactions."

Free oxides and their electroneutral compounds were assumed to be present in liquid slags because bodies of the same stoichiometric composition existed in pure crystalline form, *e.g.*, CaO or Ca_2SiO_4.

Investigations of the atomic structure of crystalline inorganic substances (oxides, silicates, phosphates, etc.) have shown that these also are composed not of neutral molecules but of ions. In his book ' The Atomic Structure of Minerals,' Bragg[2] summarizes the position as follows :

> " In the case of inorganic compounds it has become clear, largely owing to structure analysis, that we may regard the component atoms or groups of atoms as ionized in the solid state. By this is meant a redistribution of electrons amongst the atoms so that instead of being neutral they acquire positive and negative electrical charges. The forces holding the ions together are to a large extent forces of electrical attraction between oppositely charged bodies. The configuration of the structure is such that the potential energy has a minimum value. Further, the energy is mainly electrostatic. The chemical law of valency is satisfied by making the total positive and negative charges equal, but this is not brought about by pairing off individual positive and negative atoms in the structure. Each is surrounded by a number of negatives, and *vice versa* ; there are in other words no ' molecules.' "

There are no reasons to suggest that the ionic structure of inorganic substances ceases to exist in the molten state and that the ions form neutral pairs or molecules. It is probable that the rigid configurational regularity of structure is disturbed, owing to expansion and thermal agitation, but within a limited distance the co-ordination would remain practically the same as in the solid state. Certain groupings of ions which are regarded as separate structural units in solid inorganic substances can exist also as complex ions in molten silicates. These are, for instance, the stable ions SiO_4'''' and PO_4''' which have tetrahedral shape with oxygen atoms at the corners of the tetrahedra, the central atoms (Si, P) having the co-ordination number of four. This co-ordination for silicon was found in glasses (which may be regarded as undercooled liquids) by Zachariasen[3] and by Warren.[4] It was also observed by the latter that other cations in glasses, *e.g.*, K^+, Na^+, Li^+, and Ca^{++}, are surrounded on the average by 10, 6, 4, and 7 oxygens respectively ; these are also the most frequently observed co-ordination numbers of these cations in crystalline silicates. At high temperatures the co-ordination numbers may change in both crystalline and molten silicates. Bredig[5] showed that the co-ordination number of calcium in calcium orthosilicate is 6 in its low-temperature form (γCa_2SiO_4), 8 in βCa_2SiO_4, and 10 in the highest temperature forms (α and α'). There are also reasons to believe that silicon atoms in molten silicates with high silicon/oxygen ratio (acid slags, molten glass) may exist to some extent in co-ordination numbers higher than 4 ; an increase to 6 in the co-ordination number would correspond to a greater distance between the silicon cation and the surrounding anions.

The properties of molten salts and liquid slags are determined mainly by the size of ions and by the electrostatic forces acting between separate ions. That the properties of ionic melts depend largely on the size of ions is illustrated by measurements (Hildebrand and Salstrom[6]) of the activity of silver ions in molten salt mixtures containing halides of silver and alkali metals, and by measurements of viscosity of molten glasses (Endell and Hellbrügge[7]).

The ionic radii of some of the more common ions occurring in steelmaking slags, according to Pauling, (*see* also Fig. 1) are as follows :

Cations,	Å.	Anions,	Å.
Ca^{++}	0·99	O''	1·40
Mn^{++}	0·80	S''	1·84
Fe^{++}	0·75	F'	1·36
Mg^{++}	0·65	SiO_4''''	2·79
Fe^{3+}	0·60	PO_4'''	2·76
Al^{3+}	0·50		
Si^{4+}	0·41		

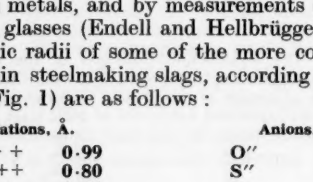


Fig. 1—Size of ions. Upper row, anions; lower row, cations. Note difference in size between Ca++ and other cations

Besides the main features arising from the relative contents of large SiO_4'''' and O'' ions, the ionic structure of liquid slags will be influenced by the concentration of Ca^{++} ions, which differ considerably in size from the other cations. Generally, the expansion of ionic structure and increased thermal agitation which accompany the process of melting permit the formation of liquid solutions from substances, for example FeO and Fe_2SiO_4, which are entirely immiscible in the solid state (*i.e.*, do not form solid solutions). In some slag mixtures, however, the tendency of ions to retain a certain co-ordination may lead to a separation of the mixture into two immiscible liquid phases. Examples of this phenomenon are discussed on page 175. From thermodynamic reasoning, ionic melts are more likely to obey the laws of ideal solutions than are aqueous solutions of electrolytes (this was first indicated by Gross[8]). However, the existing experimental data indicate that ideal behaviour is an exception rather than a rule.

* *i.e.*, in the theory of equilibria between slags and liquid steel expounded by Schenk.[1]

Investigations, mainly by Pauling,[9] on the nature of chemical bond show that a considerable part of the energy of bonding between atoms in inorganic substances that are usually regarded as ionic compounds is due to covalent linkages. This does not imply, for example, that in sodium chloride crystal or melt a certain proportion of neutral NaCl molecules is present, but implies that each sodium atom, in addition to electrostatically attracting six chlorine atoms in the lattice, also forms covalent bonds with each of the six chlorine atoms. (Similar remarks apply also to chlorine atoms.) Such considerations on the nature of chemical bond lead Pauling[10] to postulate the essential neutrality of atoms ; *namely*, that :

> " the electronic structure of substances is such as to cause each atom to have essentially zero resultant electric charge, the amount of leeway being not greater than about $\pm \frac{1}{2}$, and these resultant charges are possessed mainly by the most electropositive and electronegative atoms, and are distributed in such a way as to correspond to electrostatic stability."

The variation in the relative proportion of ionic and co-valent bonding will probably depend on the spatial distribution of atoms in the structure of liquid slag or molten salt, and may be the cause of non-ideal behaviour of atoms.

Theories explaining the behaviour of melts in terms of properties of individual atoms (ions) and of structure are not yet sufficiently developed. The description of such systems is usually completed by introducing essentially empirical factors—the so-called ' activity coefficients '—which may vary with the composition and nature of the melt. This method has been adopted also in the present paper, as the authors are fully aware that a pure ionic theory is only an approximation to the truth. It would probably be more general to describe the units of the liquid slag structure as atoms without specifying their ionic properties (electric charge, the electrostatic attractions and repulsions, etc.). However, many physical properties of slags, especially their electrical conductivity, directly indicate the existence of electrical factors which are usually considered as characteristic of ions. The authors therefore preferred to retain in this paper the terminology of ionic theory and such concepts as may be considered to give at least a plausible model of the structure of slags.

A fairly exhaustive review of literature on the electrochemical properties of slags was made in 1943 by Martin and Derge,[11] and recently by Bockris, Kitchener, Ignatowicz, and Tomlinson.[12] Those readers interested in theoretical aspects of the structure of slags and its relation to the problems of slag–metal equilibria can form a general picture of the present situation by studying the papers presented at the recent General Discussion of the Faraday Society, on the Physical Chemistry of Process Metallurgy, especially the papers by Richardson[13] and the remarks made by Guggenheim[14] at the same discussion.

Aim and Scope of the Investigation

The present investigation was undertaken with the aim of finding how far the concepts of the ionic structure could be helpful in establishing a systematic theory of slag–metal equilibria.

Recently, several valuable experimental investigations of equilibria between liquid carbon-less iron and basic slags have been published[15–21] covering a wide range of slag compositions. These experimental data have been used by the present authors to derive the fundamental relationships for slag–metal equilibria. Part II, to be published at a later date, will present the applications of the relationships to the equilibria in industrial furnaces, where the conditions are rather more complicated. Only basic slag systems are discussed, as the theoretical treatment of acid slags is more complicated by the formation of polymerized anions of varying complexity (*see* page 177), and further experimental data would be required for a satisfactory exposition of the ionic equilibria of acid slags. Some general deductions which can be applied without detailed consideration of their ionic structure are, however, discussed in later sections of this paper.

IONIC COMPOSITION OF BASIC SLAGS

The ions assumed to be present in basic slags are Fe^{++}, Fe^{+++}, Mn^{++}, Ca^{++}, Mg^{++}, SiO_4'''', PO_4''', AlO_3''', O'', S'', and F'. Since the content of oxygen atoms in basic slags in equilibrium with basic furnace walls (magnesite or dolomite) is always in excess of the amount necessary to bind silicon, phosphorus, and aluminium into the complex anions indicated above, the latter are considered to form independent units of the slag structure. The tendency of silicon and phosphorus atoms to form tetrahedral units with oxygen manifests itself in almost all crystalline silicates and phosphates, so that in the presence of an excess of oxygen ions in slag, and especially in the presence of large calcium ions, the tetrahedral anions are regarded as simple particles.

The existence of AlO_3''' ions is a more arbitrary assumption, although the theoretical calculations of Zintl and Morawietz[22] indicate that this anion should be stable in the presence of an excess of oxygen ions. With the same assumption, the relationships derived in this paper for alumina-free slags also hold equally well for systems with high-alumina slags.

The trivalent iron has been assumed to exist only in the form of Fe^{+++} ions. With normal low contents of trivalent iron, the general form of the relationships derived in this work remains the same when the existence of other ions, *e.g.*, FeO_3''', FeO_4'''' or Fe_2O_4'', is arbitrarily assumed. From purely electrostatic considerations, the stability of such complexes should be low because Fe^{+++} has a larger ionic radius and a smaller electric charge than Si or P in their respective complex anions. Variations in the activity of transition elements (Fe^{++}, Fe^{+++}, Mn^{++}) may suffice to explain their non-ideal behaviour without assuming the formation of complex anions. Recently, Chipman and Chang[23] assumed the existence of Fe_2O_5'''' ions mainly because the di-calcium ferrite occurs as a crystalline phase. The present authors regard this assumption as quite arbitrary and unnecessarily complex. The stoichiometric composition of a crystalline phase cannot be considered as a reliable indication of the actual structure, and it is improbable that Fe_2O_5 groupings occur as structural

units of solid di-calcium ferrite. As, according to Chipman and Chang, the Fe_2O_5'''' ion must be endowed with a highly variable activity coefficient to explain its behaviour, the assumption of Fe_2O_5'''' ions offers no advantage over that of simple Fe^{+++} ions.

Method of Calculating the Ionic Composition of Slag

The method of calculating the slag composition in terms of ionic fractions may be outlined as follows : First, the number of mols per 100 parts by weight is calculated by dividing the weight percentage of each oxide by the corresponding molecular weight. Each mol of a metallic oxide (CaO, FeO, MnO, MgO) contributes one cation and one oxygen ion, and each mol of Fe_2O_3 contributes two cations and three oxygen ions. Each mol of SiO_2 consumes two oxygen anions in the formation of SiO_4'''' ion ; similarly, three ions of oxygen are consumed in the formation of $2PO_4'''$ or $2AlO_3'''$ from each mol of P_2O_5 or Al_2O_3. The difference between the oxygen ions supplied by metallic oxides and those consumed in the formation of SiO_4'''', PO_4''', and AlO_3''', represents the amount of free uncombined oxygen ions. The number of g. ions of each separate ion in 100 parts by weight, divided by the total number of ions, N, gives the ionic fraction of the corresponding ion in the slag.

Although atoms in liquid steel may also be in the ionic state, there is little purpose in extending the ionic theory to the metal, since this can usually be considered as a dilute solution for which the laws of ideal solutions are applicable ; the atomic (ionic) or weight concentrations of elements in the liquid metal will thus be proportional to their activity. In the calculations of equilibria in this paper, therefore, the weight percentages have been used for the elements dissolved in the metal phase. At the same time, the possibility of changes in activity coefficient must be borne in mind, and in fact those caused by carbon in liquid steel will be given in Part II.

Method of Expressing the Equilibria

When liquid iron containing manganese, etc., is in contact with liquid slag containing Fe^{++} and Mn^{++}, etc., it can be deduced from the principles of electrochemical potential[24, 25, 26] that the simultaneous equilibria of two reactions, for example :

$$Fe - 2 \text{ electrons} = Fe^{++}$$
$$Mn^{++} + 2 \text{ electrons} = Mn$$

or

$$Fe + Mn^{++} = Mn + Fe^{++},$$

are characterized by the ratio :

$$k_{Mn}^{Fe} = \frac{[Mn](Fe^{++})}{(Mn^{++})[Fe]}$$

As explained earlier, it is hardly possible that liquid slag should have all the properties of ideal solutions ; the characteristic value k may therefore vary with the slag composition. Consequently, the authors prefer to define this value as an equilibrium ratio, without using the term ' constant.' The German workers use the term ' die Kennzahl ' which does not necessarily involve the notion of constancy of k-values. The k-values would be constant (by definition) if activities were used instead of concentrations. In the following exposition, the equilibrium ratios of concentrations are expressed by small letter k, and equilibrium constants (ratios of activities) by capital letter K.

When the reactions are expressed in the reverse direction, *e.g.*, $Mn + Fe^{++} = Fe + Mn^{++}$, the equilibrium ratio is reversed :

$$\frac{[Fe](Mn^{++})}{[Mn](Fe^{++})} = k_{Fe}^{Mn}$$

The usual convention in chemical thermodynamics is to write the reaction equation and the equilibrium constant in a manner such that the reaction proceeding from left to right is exothermic and the concentrations corresponding to the right side of the reaction equation are in the numerator of the equilibrium constant. However, since the heat of the reaction is not always known, it is more convenient to attach subscript and superscript letters to the equilibrium value to indicate the direction of the reaction equation under consideration. The reversal of subscript and superscript of a k-value would correspond to a reversal of the reaction equation. Thus, for example,

$$k_{Mn}^{Fe} = \frac{1}{k_{Fe}^{Mn}}$$

The superscript of a k-value indicates that the concentration of the element in question in the metallic phase is in the denominator of the equilibrium ratio corresponding to the left side of the reaction equation. Thus, for example, for the reactions

$$\underline{Fe} + \underline{O} = Fe^{++} + O''$$
$$\underline{O} + S'' = O'' + \underline{S}$$

where the underlined symbols relate to the metal phase,

$$k_O^{Fe} = \frac{(Fe^{++})(O'')}{[Fe][O]}$$

and

$$k_S^O = \frac{[S](O'')}{[O](S'')}.$$

Since the ideal mass action law has not been assumed valid for each equilibrium, the dependence of the equilibrium ratio on the content of each slag constituent has been investigated. It was found, generally, that the principal equilibrium ratios are functions of only one component of the slag. An explanation of these empirical functions has been given in those instances where the present knowledge of the properties of ionic melts permits general conclusions to be drawn.

Effect of Errors in Experimental Technique

The accuracy of the calculation for the ionic concentration of a slag constituent and for the equilibrium ratios is influenced by several factors, the most important being (i) the extent of deviation from the equilibrium, and (ii) the accuracy of sampling technique and chemical analysis. Since the concentration of uncombined oxygen anions is obtained by subtracting figures of the same order of magnitude, the calculated values of the oxygen ion content are most sensitive to experimental errors. Therefore a large number of experimental points is required, to obviate the effects of such errors. In addition to the possible error in chemical analysis, especially in the determination of elements present in small concentrations,

significant errors may also arise when the slags are not homogeneous, *e.g.*, when they contain a suspension of solid oxide phase. This condition may arise either from unfluxed slag constituents or by precipitation of solid phases. Thus Chipman, Winkler, and Grant[15, 16] carried out their experiments in magnesia crucibles in induction furnaces; the slag was also heated from above by an electric arc, and the melts were subject to considerable variation in temperature between successive test samples. Since the solubility of MgO decreases with decreasing temperatures, samples taken after a lowering of the temperature may show, on analysis, excessive amounts of MgO, and the calculated O″-ion contents would be too high.

The foregoing considerations may be illustrated by data from Winkler and Chipman's paper.[15] Thus, Mg^{++} and O″ ions—which possess an electronic structure similar to that of rare gases—are likely to behave as ideal particles, and therefore, for slags saturated with solid MgO, the product $(Mg^{++})(O'')$ would be expected to be constant for constant temperature. The values of this solubility product, determined from the tests of Winkler and Chipman, are shown in Fig. 2. The constancy of the product $(Mg^{++})(O'')$ is quite satisfactory, considering the indicated sources and effects of experimental errors; its value varies only slightly with temperature. Figure 3 shows the plot of Mg^{++} contents against the O″ content for the mean temperature of 1600° C. (± 30° C.). Those melts for which the points deviated considerably above the isotherm in Fig. 3 also gave abnormal values for other equilibrium ratios (*see* later). Thus the presence of suspended magnesium oxide affects the accuracy of calculated equilibrium ratios in which oxygen ions take part. In those tests in which the content of Mg^{++} ions was considerably below the isotherm in Fig. 3, equilibrium between slag, metal, and crucible evidently had not been reached, and therefore the equilibrium ratios for these melts also deviate from the mean values. Such experimental errors, however, are compensated to a great extent by the large number of tests investigated.

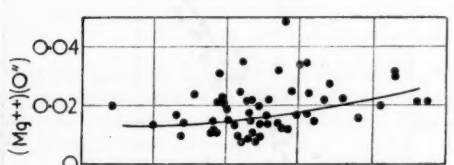


Fig. 2

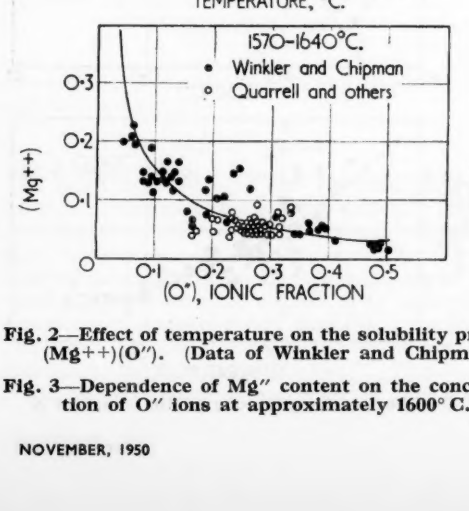


Fig. 3

Fig. 2—Effect of temperature on the solubility product $(Mg^{++})(O'')$. (Data of Winkler and Chipman)

Fig. 3—Dependence of Mg″ content on the concentration of O″ ions at approximately 1600° C.

It is most unlikely that the content of oxygen ions in slags in equilibrium with the basic crucible (*i.e.*, MgO) could fall below a certain low value, *i.e.*, that the slag could become acid. For this investigation, therefore, those experiments in which the amount of acids (SiO_2, P_2O_5, Al_2O_3, etc.) was in excess of that necessary to bind all basic oxides (FeO, MnO, CaO, MgO) to salts of the type Me_2SiO_4, $Me_3(PO_4)_2$, $Me_3(AlO_3)_2$, were regarded as deviating from equilibrium, and were not taken into consideration. This relates particularly to the series E.35 by Chipman and Winkler, and to a few other samples.

In the experiments of Balajiva, Quarrell, and Vajragupta[18] the samples were melted by an electric arc in a laboratory magnesia-lined furnace. The agitation of melts was less violent than with induction heating, and consequently less erosion of magnesia from the furnace walls would be expected. Moreover the temperature of their melts was more uniform, so that deviations due to experimental technique are less evident in their results. Unfortunately Quarrell and co-workers gave only the phosphorus contents of the metal baths, so that their data are limited to the consideration of phosphorus and trivalent iron equilibria.

THE EQUILIBRIA OF SULPHUR AND OXYGEN

The principal reactions governing the equilibrium distribution of sulphur and oxygen between slag and metal are:

$$\underline{O} + 2 \text{ electrons} = O''$$
$$S'' - 2 \text{ electrons} = \underline{S}$$

The total reaction is therefore:

$$\underline{O} + S'' \rightleftharpoons O'' + \underline{S} \quad \text{.....(1)}$$

From the data of Chipman, Winkler, and Grant, numerical values of the equilibrium ratio:

$$k_S^O = \frac{[S](O'')}{[O](S'')} \quad \text{.....(2)}$$

have been calculated. It was found that, within the limits of experimental errors, the ratio k_S^O is independent of the concentration of slag constituents, especially of O″, SiO_4'''', and Ca^{++} ions. Since, as already mentioned, ideal behaviour of liquid slags has not been assumed, the observed constancy of the k_S^O ratio is regarded at this stage as an empirical result.

Equation (2) was derived first by Samarin, Temkin, and Shvarzman,[27] who used the data of Fetters and Chipman.[17] A detailed discussion of the relationship was given recently by Carter.[28]

According to the ionic theory, the rational measure of the basicity of slags is the content of uncombined oxygen anions. The sulphur–oxygen equilibrium ratio is thus independent of the ionic basicity of slags and of the content of Ca^{++} or other ions, and can therefore be regarded as an equilibrium which obeys the ideal

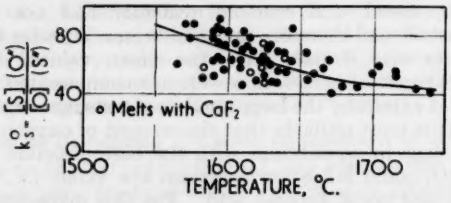


Fig. 4—Effect of temperature on the equilibrium ratio k_S^O

mass action law. The ideal behaviour of O″ and S″ ions is probably the result of the stability of their electronic structure, which is similar to that of neon for the oxygen ion, and of argon for the sulphur anion. Other equilibria discussed in the following sections deviate considerably from the ideal mass action law; the reaction $\underline{O} + S'' = \underline{S} + O''$ is thus rather exceptional.

Figure 4 shows that the value of the equilibrium ratio:

$$k_S^O = \frac{[S](O'')}{[O](S'')} = 70 \text{ at } 1600^\circ \text{ C.} \quad \ldots\ldots\ldots\ldots(3)$$

tends to decrease with increasing temperature. A few tests made with addition of CaF_2 (indicated by open circles in Fig. 4) fall within the spread of other results. The equation of the curve drawn through the points in Fig. 4 can be represented by the following formula:

$$\log k_S^O = \frac{6500}{T} - 2{\cdot}625 \quad \ldots\ldots\ldots\ldots\ldots\ldots(4)$$

It is thus seen that the reaction is exothermic ($-\Delta H = 30$ kg.cal.). At a constant (O″)/[O] ratio, the desulphurization of metal (*i.e.*, the ratio (S″)/[S]) increases with increasing temperature.

Chipman and Grant[16] have obtained good correlation between (S)/[S], expressed in weight per cent, and the 'excess of base,' which was obtained as follows:

All slag analyses were converted first to mols, and combinations of base or acid for neutralization were taken on a molar basis, *e.g.*,

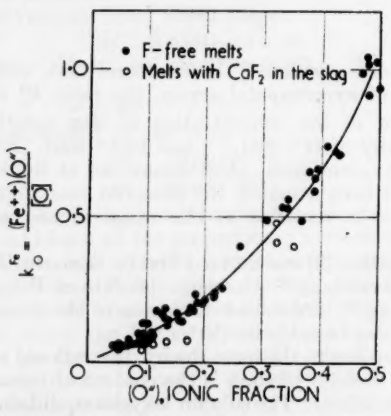


Fig. 5—Dependence of k_O^{Fe} on the content of (O″). (Data of Winkler and Chipman; temperature 1570–1640° C.)

2 Base : 1 SiO_2
4 Base : 1 P_2O_5
2 Base : 1 Al_2O_3
1 Base : 1 Fe_2O_3

FeO and CaF_2 were considered to be neutral species. CaO, MnO, and MgO were considered as basic constituents of equal value mol per mol; Fe_2O_3 was assumed to behave as an acid only as long as there was base available. Chipman and Grant's 'excess of base' factor was to a certain extent analogous to the content of oxygen ions according to the ionic theory. The practical significance of their work was that it demonstrated conclusively that there is no specific difference between various bases (CaO, MnO, MgO) with regard to the desulphurization. Their method was incomplete, however, since they did not regard FeO as a 'base,' and they neglected the rôle of oxygen dissolved in steel in the desulphurization reaction.

THE EQUILIBRIUM $Fe + O = Fe^{++} + O''$

This reaction, which summarizes the two equilibria

$$\underline{Fe} - 2 \text{ electrons} = Fe^{++}$$
$$\underline{O} + 2 \text{ electrons} = O'',$$

gives information on the relationship between the contents of divalent iron in the slag and oxygen in the metal.

Fig. 6—Correlation between log k_O^{Fe} and log (O″)

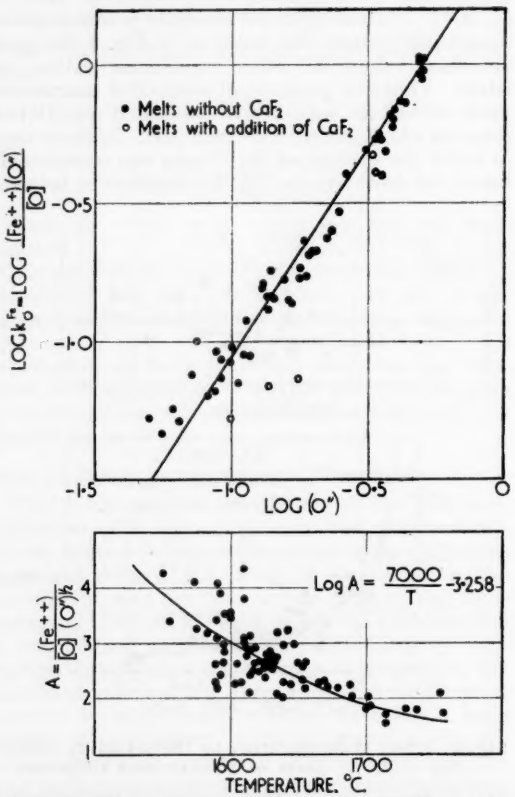


Fig. 7—Effect of temperature on the constant *A*

The equilibrium ratio:

$$k_O^{Fe} = \frac{(Fe^{++})(O'')}{[O]} \quad \ldots\ldots(5)$$

of this reaction depends on the content of O'' ions (Fig. 5). Plotting log k_O^{Fe} against log (O'') at a practically constant temperature (1590–1640° C.), a straight line is obtained (*see* Fig. 6) which can be represented by the equation:

$$\log k_O^{Fe} = \frac{3}{2}\log (O'') + \log 3 \quad \ldots\ldots(6)$$

Or, generally:

$$k_O^{Fe} = \frac{(Fe^{++})(O'')}{[O]} = A(O'')^{3/2}, \quad \ldots\ldots(7)$$

where A is a constant depending on temperature only. The variation of constant A with temperature can be represented by the equation:

$$\log A = \frac{7000}{T} - 3{\cdot}258 \quad \ldots\ldots(8)$$

(*See* Fig. 7.)

A few tests made with the addition of calcium fluoride (indicated by open circles in Figs. 5 and 6) show a tendency to be lower than the points for fluoride-free tests. It is evident that fluoride ions increase the activity coefficient of ferrous ions. Unfortunately, this effect could not be examined quantitatively, because of the limited experimental data.

The simple empirical relationship given in equation (7) reflects some fundamental property of ferrous ions in basic slags. On page 173 it was shown that oxygen ions behave as ideal particles in sulphur–oxygen equilibrium in basic slags. The strong dependence of the ratio k_O^{Fe} on the content of oxygen ions must therefore be ascribed to the variation in the activity coefficient of ferrous ions, which become more inert in slags with high O''-ion content.

When using the activities of reacting particles, the equilibrium is characterized by a true equilibrium constant. Thus, the expression:

$$\frac{a_{Fe^{++}} a_{O''}}{[O]} = K \quad \ldots\ldots(9)$$

must be constant (at constant temperature). Since oxygen anions behave as ideal particles, their activity is equal to their ionic concentration. The activity of ferrous ions is: $a_{Fe^{++}} = f_{Fe^{++}}(Fe^{++})$ where $f_{Fe^{++}}$ is the activity coefficient of Fe^{++} ions, so that equation (9) may be represented thus:

$$\frac{f_{Fe^{++}}(Fe^{++})(O'')}{[O]} = K \quad \ldots\ldots(10)$$

Comparison of equations (7) and (10) shows that K will be constant if:

$$f_{Fe^{++}} = \frac{K'}{(O'')^{3/2}} \quad \ldots\ldots(11)$$

It must be pointed out that the variability of the activity coefficient of ferrous ions might be primarily associated not with the effect of oxygen ions but with that of complex anions (SiO_4'''' and PO_4''') present in the slags under discussion. There is a simple linear relationship between the content of O'' ions and the sum of the contents of SiO_4'''' and PO_4''' (*see* Fig. 8*a*). The ratio k_O^{Fe} can therefore be represented as a function of the sum $SiO_4'''' + PO_4'''$. This is shown in Fig. 8*b*, for the same data as in Fig. 5. For practical

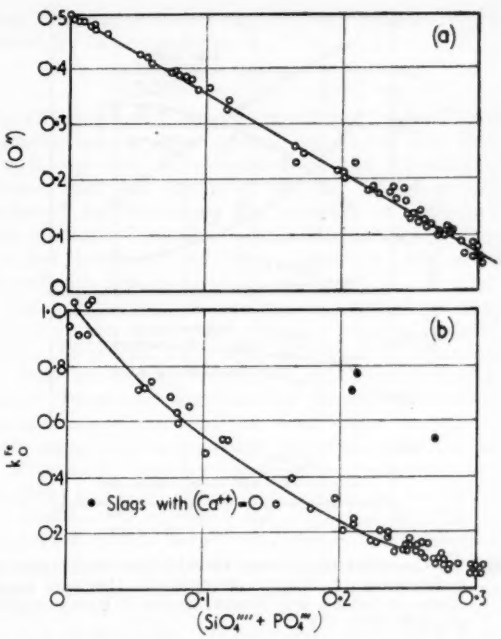


Fig. 8—(*a*) Relationship between (SiO_4'''' + PO_4''') and (O'') for basic slags. (*b*) Dependence of k_O^{Fe} on content of (SiO_4'''' + PO_4'''). (Data of Winkler and Chipman; temperature 1570–1640° C.)

reasons the authors prefer to use the empirical equation (7) derived from Fig. 5, because it is more simple than the mathematical expression for the equation of the curve in Fig. 8*b*.

Further confirmation of the above relationships can be derived from the experimental investigation of the equilibrium between two immiscible slags, carried out by Oelsen and co-workers.[20, 21] These authors observed that when melted in iron crucibles some mixtures of FeO–CaO–P_2O_5 and FeO–Na_2O–P_2O_5 separate into two immiscible slag layers, the lower layer being richer in CaO (or Na_2O) and P_2O_5. Two immiscible slag layers were obtained also from mixtures of calcium fluoride with iron oxide alone or with additions of phosphates and silicates. The present authors have calculated the compositions of their slags in terms of ionic fractions, assuming, as before, the existence of the ions: Fe^{++}, Fe^{+++}, Ca^{++}, Na^{+}, Mn^{++}, PO_4''', SiO_4'''', and F'. The variations in the ionic compositions of the two layers of the system FeO–CaO–P_2O_5 at 1400–1420° C. are illustrated in Fig. 9, in which the ionic fractions are plotted against the concentration of Ca^{++} ions in the upper layer. (This graphical presentation is permissible because the system contained four components (Fe, Ca, O, P) and three phases (solid iron, two slag layers), and is therefore monovariant, *i.e.*, at constant temperature and pressure.)

Since the two layers contain Fe^{++} and O'' ions, an equilibrium exists which is characterized by the equation:

$$\overline{Fe^{++}} + \overline{O''} = \overline{\overline{Fe^{++}}} + \overline{\overline{O''}},$$

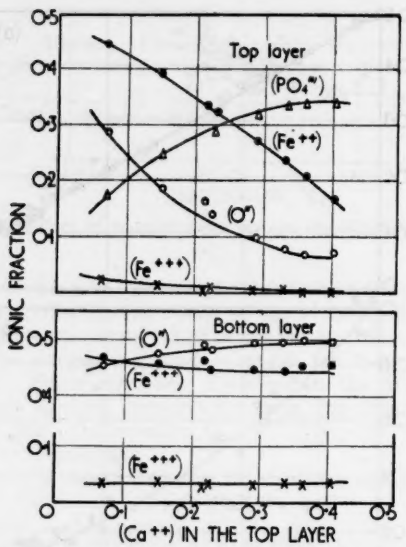


Fig. 9—Composition of two immiscible slag layers as a function of (Ca++) content in the top layer. (Data of Oelsen and Maetz; melts in iron crucibles at 1400–1440° C.)

where the single line above the symbol refers to the bottom layer, and the double line to the top layer. The equilibrium ratio is given by the formula :

$$k_{\mathrm{I}}^{\mathrm{II}} = \frac{\overline{\overline{(\mathrm{Fe^{++}})}}\,\overline{\overline{(\mathrm{O''})}}}{\overline{(\mathrm{Fe^{++}})}\,\overline{(\mathrm{O''})}} \quad \ldots\ldots\ldots\ldots\ldots\ldots (12)$$

Referring to Fig. 9, it will be seen that the contents of $\overline{\mathrm{Fe^{++}}}$ and $\overline{\mathrm{O''}}$ in the bottom layer change only very slightly over a wide range of upper slag Ca^{++}-ion contents, so that the product $\overline{(\mathrm{Fe^{++}})}\overline{(\mathrm{O''})}$ for the lower layer is practically constant. By plotting the logarithm of the equilibrium ratio k^{II}, against the logarithm of the oxygen ion content in the top layer, a straight-line relationship is found which holds remarkably well over a broad range of O'' contents. Figure 10 shows the data for the mixtures FeO(MnO)–CaO–P_2O_5, FeO–Na_2O–P_2O_5. The dependence of $k_{\mathrm{I}}^{\mathrm{II}}$ on $\overline{\overline{(\mathrm{O''})}}$ is given by the formula :

$$k_{\mathrm{I}}^{\mathrm{II}} = A'\overline{\overline{(\mathrm{O''})}}^{3/2}, \quad \ldots\ldots\ldots\ldots\ldots\ldots (13)$$

which is analogous to and therefore confirms equation (7).

The fact that the ratio $k_{\mathrm{I}}^{\mathrm{II}}$ depends only on the O'' content indicates that the activity coefficient of ferrous ions is not influenced by Ca^{++} or Na^{+} ions. It is interesting to note that the equilibrium ratio $k_{\mathrm{I}}^{\mathrm{II}}$ for the FeO–CaO(Na_2O)–P_2O_5 mixtures investigated by Oelsen and co-workers* reaches a critical point at which the immiscibility disappears (*i.e.*, when $\log k_{\mathrm{I}}^{\mathrm{II}} = 0$), always at the same content of oxygen ion (at constant temperature). This critical (O'') content is approximately 0·5 at 1410–1450° C.

The empirical equation (7) leads to a calculation of the oxygen content of metal from the analysis of slag. Thus :

$$[\mathrm{O}] = \frac{(\mathrm{Fe^{++}})}{A(\mathrm{O''})^{\frac{1}{2}}} \quad \ldots\ldots\ldots\ldots\ldots\ldots (14)$$

This equation is of considerable importance to the practice of steelmaking ; it can be related to other equilibria, and will be discussed in detail in Part II, dealing with applications of ionic theory to practical steelmaking.

There have been many attempts to correlate the content of divalent iron in slag with the oxygen content of the metal, based on the assumption that there is a partition ratio of iron oxide between slag and metal. The ratio (FeO)/[O] thus characterized the state of oxidation of the system. It was found in practice that this ratio depended largely on the slag composition ; however, the variability was attributed to the formation of molecular compounds (between acids and bases), which affects either the amount of free iron oxide available for distribution or the actual molar concentration of iron oxide. Thus, Taylor and Chipman[29] assumed the formation of double molecules of calcium orthosilicate $(Ca_2SiO_4)_2$, but the wide spread in their results did not justify this assumption or their conclusions regarding the partition of iron oxide.

According to the ionic theory of slags, the term ' distribution of iron oxide between slag and metal ' has no significance, since the iron oxide does not exist in molecular form. The equilibrium ratio :

$$k_{\mathrm{O}}^{\mathrm{Fe}} = \frac{(\mathrm{Fe^{++}})(\mathrm{O''})}{[\mathrm{O}]}$$

would have a formal similarity with the ' iron oxide distribution ratio ' only in the extreme examples :

(*a*) for ternary systems Fe–Ca–O, Fe–Mg–O, Fe–Mn–O (*i.e.*, pure iron containing oxygen and manganese in equilibrium with a ferrous oxide slag containing admixtures of CaO, MnO, or MgO)

(*b*) for the pure systems Fe–Si–O and Fe–Mn–Si–O (*i.e.*, pure iron containing silicon, manganese, and

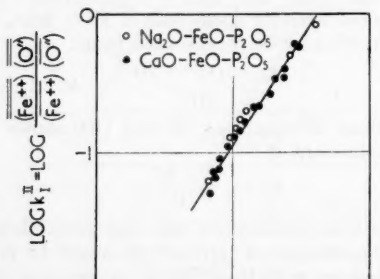


Fig. 10—Dependence of distribution ratio $k_{\mathrm{I}}^{\mathrm{II}}$ on the O'' content of the top slag layer for immiscible slags in the systems Na_2O–FeO–P_2O_5 and CaO–FeO–P_2O_5. (Data of Oelsen and co-workers; melts in iron crucibles)

* The values of the equilibrium ratio $k_{\mathrm{I}}^{\mathrm{II}}$ for mixtures containing calcium fluoride are considerably lower than those shown in Fig. 15*b*. It can be deduced from the work of Oelsen and co-workers[20, 21] that fluoride ions strongly increase the activity coefficient of ferrous ions. Moreover, the formation of complex ions with phosphate ions is not excluded.

oxygen in equilibrium with solid silica and acid slags).

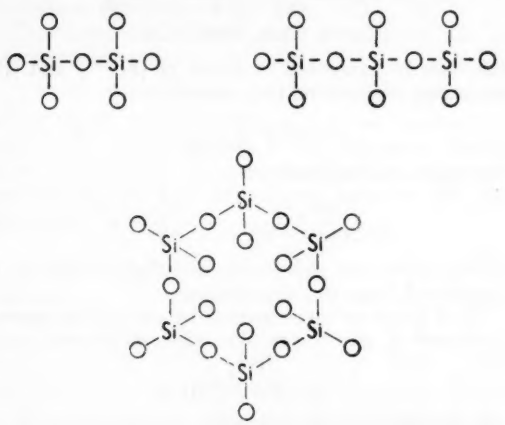
In both instances the content of oxygen ions is constant.

It has been shown by several workers that, in acid slags saturated with silica, the analysed content of ferrous oxide can be correlated directly with the oxygen content of the steel, such that :

$$\frac{(FeO)}{[O]} = \text{Constant.}$$

This expression could be derived from the equilibrium ratio K_O^{Fe}, if (O'') is constant. It is impossible at present to state definitely the value of the oxygen ion concentration in acid slags without further assumptions on the ionic structure of acid slags (*see* later), but it appears that the concentration of (O'') ions in acid slags has a very low but constant value.

The complexity of the ionic structure of acid slags is indicated by studies on glass, in which it has been shown that SiO_4 tetrahedra polymerize to yield larger ions in which oxygen atoms are shared between two silicon atoms : examples of this structure are shown below :



Chains or networks of polymerized anions may exist in acid slags, but as the extent of such formation is not known it is impossible to calculate the total number of ions, N, and the ionic fractions for constituents of acid slags, according to the method used in this paper.

As will be discussed also on p. 180, the stability of simple or polymerized complex ions and the distance between the central silicon atoms and oxygen atoms in silicon tetrahedra will depend on the electrostatic action of cations surrounding the complexes. Cations having small ionic radius (Fe^{++}, Mn^{++}, Mg^{++}) will attract oxygen atoms in the complex more strongly than large Ca^{++} ions. This may lead to readjustment of SiO_4 units in liquid slag in a manner such that the resulting structures will have smaller density of the negative electric charge on their periphery. In other words, simple silicate tetrahedra should show tendency to polymerize even in slag with high content of O'' ions, if small cations (Fe^{++}, Mn^{++}, Mg^{++}) are present in larger concentration than that of calcium ions. The polymerization reactions can be represented by the equations :

$$2\,SiO_4'''' = Si_2O_7'''' + O''$$
$$3\,SiO_4'''' = Si_3O_{10}'''''' + 2\,O'', \text{ etc.}$$

The effect of cationic environment on the stability of complex anions was suggested by Endell and Hellbrugge[7] in their investigation on the viscosity of glasses, and was discussed by one of the present authors[30] in relation to the stability of phosphate ions in steelmaking slags. An independent and more detailed treatment of these problems was given recently by Esin.[31, 32]

The polymerization reactions written above may lead to an increase in the content of oxygen ions, O'', but in the present state of knowledge it is impossible to state exactly the extent of the polymerization. Esin[31, 32] assumed, and this has been followed in the present paper, that calcium ions, when present in basic slags in greater amount than twice the number of SiO_4 units, entirely suppress the polymerization reactions indicated above. Therefore, the content of O'' ions can be obtained by calculations similar to those used in this work. This assumption is justified by the fact that the relationship deduced in this paper for k_O^{Fe} ceases to be valid when calcium ion content is considerably smaller than one-half of the content of SiO_4 ions. Three points shown in Fig. 8*b* as black circles indicate the k_O^{Fe}-values for basic slags containing no calcium ions (derived from the measurements of Taylor and Chipman in rotating liquid iron crucibles). These values illustrate the extent of the deviation for this extreme case. The available experimental data are not yet sufficient to determine exactly the $(Ca^{++})/(SiO_4'''')$ ratio at which the deviations from the empirical curve of k_O^{Fe}-values exceed the range of experimental errors. Examination of the data of Winkler and Chipman[15] and of Fetters and Chipman[17] leads to the conclusion that the deviations can be entirely neglected when the content of calcium ions is equal to that of SiO_4'''' ions. The authors accept, therefore, that the relationships derived in this paper are valid for those slags in which the ratio $(Ca^{++})/(SiO_4'''') \geqslant 1$. This covers practically the whole range of basic open-hearth slags.

THE EQUILIBRIUM $Fe + S = Fe^{++} + S''$

This equilibrium is of a type similar to the equilibrium $Fe + O = Fe^{++} + O''$. Its equilibrium ratio :

$$k_S^{Fe} = \frac{(Fe^{++})(S'')}{[S]} \quad \ldots\ldots(15)$$

is therefore expected to depend on the content of (O'') ions. This relationship is shown by the plot of points in Fig. 11*a*, from which a quantitative expression (which is practically independent of temperature) may be derived, as follows :

$$k_S^{Fe} = B(O'')^{3/2} \quad \ldots\ldots(16)$$

where $B = 0{\cdot}043$.

The sulphur distribution ratio is therefore given by the expression :

$$\frac{(S'')}{[S]} = \frac{B(O'')^{3/2}}{(Fe^{++})} \quad \ldots\ldots(17)$$

from which several practical points are evident. Thus, desulphurization of steel increases proportionally to

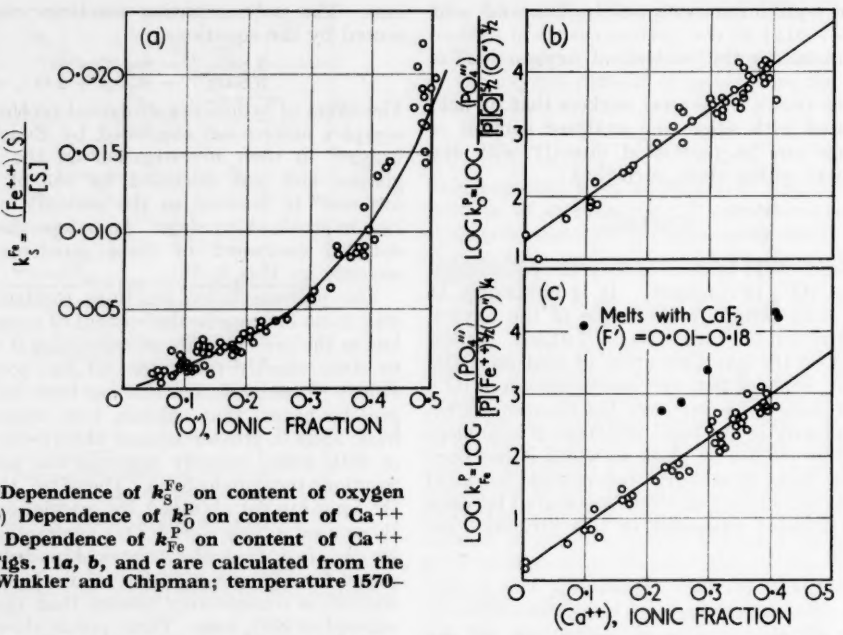


Fig. 11—(*a*) Dependence of k_S^{Fe} on content of oxygen ions. (*b*) Dependence of k_O^P on content of Ca++ ions. (*c*) Dependence of k_{Fe}^P on content of Ca++ ions. (Figs. 11*a*, *b*, and *c* are calculated from the data of Winkler and Chipman; temperature 1570–1640° C.)

the power 3/2 of free oxygen ion content (which is the measure of the ionic basicity), and is inversely proportional to the content of ferrous ions. Conditions leading to an increase of the ionic basicity of slag and to a simultaneous decrease of ferrous ions in slag would favour the desulphurization.

Examples of the applications of these relationships to furnace data will be given in Part II.

EQUILIBRIA OF PHOSPHORUS

The simplest reaction scheme for the equilibrium of transfer of phosphorus from metal to slag can be represented by the following equation :

$$2\,\underline{P} + 5\,\underline{O} + 3\,O'' = 2PO_4''' \quad \text{.....(18)}$$

The equilibrium ratio of this reaction is :

$$\left(k_O^P\right)^2 = \frac{(PO_4''')^2}{[P]^2[O]^5(O'')^3} \quad \text{.....(19)}$$

It is more convenient, however, to use the square root of this expression, *viz.* :

$$k_O^P = \frac{(PO_4''')}{[P][O]^{5/2}(O'')^{3/2}}, \quad \text{.....(20)}$$

since this expression leads directly to a phosphorus distribution ratio :

$$\frac{(PO_4''')}{[P]} = k_O^P[O]^{5/2}(O'')^{3/2} \quad \text{.....(21)}$$

The values of k_O^P calculated from the data of Chipman and Winkler were found to depend only on the content of Ca++ ions. Figure 11*b* shows that log k_O^P is a linear function of the Ca++-ion content, and that it can be expressed by the formula :

$$\log k_O^P = 7(Ca^{++}) + \log C_O^P = 7(Ca^{++}) + 1{\cdot}35 \quad \text{...(22)}$$

Considering the very wide range of slag compositions and the indirect evaluation of the O″ content, the agreement of the various experimental data with equation (22) can be regarded as quite satisfactory.

The content of oxygen in metal, [O], in equation (20) can be expressed in terms of (Fe++) and (O″) according to equation (14), namely :

$$[O] = \frac{(Fe^{++})}{A(O'')^{\frac{1}{2}}}.$$

This gives an expression :

$$\frac{(PO_4''')}{[P]\,(Fe^{++})^{5/2}(O'')^{\frac{1}{2}}} = \frac{k_O^P}{A^{5/2}} = k_{Fe}^P \quad \text{.....(23)}$$

which allows the phosphorus distribution ratio to be calculated from the slag analysis.

In a previous investigation by one of the present authors[26] it was shown that the equilibrium ratio

$$\frac{(PO_4''')}{[P]\,(Fe^{++})^{5/2}(O'')^4}$$

corresponding to the reaction

$$\underline{P} + \frac{5}{2}Fe^{++} + 4\,O'' = PO_4''' + \frac{5}{2}\underline{Fe}$$

depended strongly on the content of both Ca++ and O″ ions. The above ratio would be a true constant when the activities were used instead of ionic fractions. The present investigation shows that the activity coefficient of PO_4'' ions depends only on the content of Ca++ ions, and that the activity coefficient of Fe++ ions depends only on the content of O″ ions. The variation of the activity coefficient of Fe++ ions with the content of O″ ions is accounted for in the above deduction of equation (23), so that the ratio k_{Fe}^P should depend only on the content of Ca++ ions.

From equations (22) and (23) :

$$\log k_{Fe}^P = \log k_O^P - \frac{5}{2}\log A = 7(Ca^{++}) + 1{\cdot}35 - \frac{5}{2}\log A$$

The values of k_{Fe}^P calculated from the data of Winkler and Chipman[15] are in satisfactory agreement with the above formula (*see* Fig. 11*c*).

Equation (23) has been applied also to the experimental data of Balajiva, Quarrell, and Vajragupta.[18, 19]

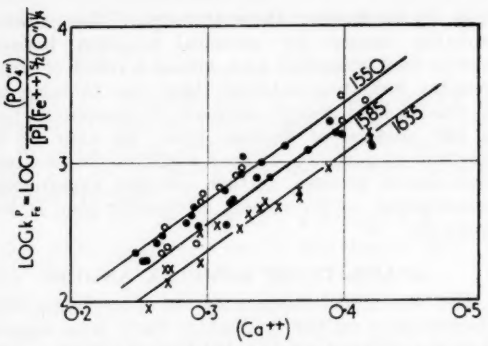


Fig. 12—Dependence of log k^P_{Fe} on (Ca++) and temperature. (Data of Quarrell and co-workers)

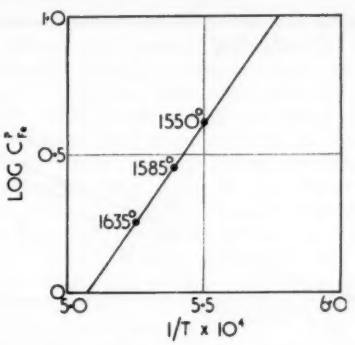


Fig. 13—Dependence of log C^P_{Fe} on temperature

Figure 12 represents the plot of log k^P_{Fe} for their melts at three temperatures, against the content of Ca++ ions. These points show a smaller spread than the data of Winkler and Chipman. As indicated earlier, this is considered to be the result of better approach to equilibrium ; the values of k^P_{Fe} derived from the data of Quarrell and his co-workers are therefore considered rather more accurate.

The dependence of log k^P_{Fe} on (Ca++) can be expressed generally in the form :

$$\log k^P_{Fe} = 7(Ca^{++}) + \log C^P_{Fe}, \quad \ldots\ldots(24)$$

where C^P_{Fe} is a constant depending on temperature only. The average values of log C^P_{Fe} when plotted against reciprocal absolute temperature fall on a straight line (*see* Fig. 13), so that equation (24) can be written :

$$\log k^P_{Fe} = 7(Ca^{++}) + \frac{14{,}660}{T} - 7{\cdot}44 \quad \ldots\ldots(25)$$

Values of log C^P_{Fe} calculated for several temperatures are as follows :

T, ° C.	1500	1550	1575	1600	1625	1650
Log C^P_{Fe}	0·83	0·610	0·484	0·390	0·275	0·196

The concentration of oxygen anions occurs to the power of $\frac{1}{4}$ in equation (23) ; this suggests that, within the range of O'' concentrations usually found in the basic open-hearth process (0·10–0·30 (O'')), variations in the ionic basicity of slags would have little influence on the value of k^P_{Fe} (approximately ± 10%). In approximate calculations, therefore, the term $(O'')^{\frac{1}{4}}$ can be neglected, and equation (23) can be simplified as follows :

$$k'^P_{Fe} = \frac{(PO_4''')}{[P](Fe^{++})^{5/2}} \quad \ldots\ldots(26)$$

The plot of 2 log k'^P_{Fe} against the ionic fraction of Ca++ ion gives an approximately straight line (in the region 0·20–0·50 ion for Ca++) which can be represented by the equation :

$$2\log k'^P_{Fe} = \log\left\{\frac{(PO_4''')^2}{[P]^2(Fe^{++})^5}\right\} = 14(Ca^{++}) + \text{constant}' \quad \ldots(27)$$

Almost the same form of equation was put forward by Quarrell and his co-workers, who represented their results by the empirical formula :

$$\log K = \log\frac{(P_2O_5)}{[P]^2(FeO)^5} = 13{\cdot}6\log(CaO) - 25{\cdot}97, \ldots(28)$$

in which molar percentage concentrations were used. The total number of mols per 100 parts of slag varied within a comparatively narrow range, the deviation from average being ± 10%. In view of the possible sources of such deviations a 10% deviation is not large, so that the total number of mols could be regarded as approximately constant. The molar ionic concentrations for their slags would therefore be approximately proportional to the analytical contents of components, and a straight-line relationship of the type shown would be obtained in both cases.

According to Quarrell and co-workers, log$K$ depends on the *logarithm* of the calcium (oxide) concentration, whereas the authors' diagrams indicate simple linear dependence of log k^P_{Fe} on the calcium (ion) concentration. By plotting the values of log$K$, as found by Quarrell and co-workers, against the molar fraction of calcium oxide, a straight-line relationship is obtained with a spread of points similar to that obtained when plotting log$K$ against the *logarithm* of calcium oxide, for the range of CaO contents (30–60% CaO) in their experiments. The equation of the line is approximately :

$$\log K = 14(CaO) + \text{constant}'' \quad \ldots\ldots(29)$$

Since CaO ~ (Ca++), there is close similarity between equations (27) and (29). However, the relation between log$K$ and log(CaO) as suggested by Quarrell in equation (28) is of limited validity, and cannot fit the data of Winkler for low contents of calcium and oxygen ions in slag. The same limitation applies, of course, to the authors' equations (26) and (27) which, as stated above, are only approximations of the general equation (23).

INFLUENCE OF FLUORIDE IONS ON THE EQUILIBRIA

The foregoing deductions apply strictly only to systems without fluoride ions in the slag. Winkler and Chipman investigated only a few melts with the addition of 10–20% of calcium fluoride to the slag. On the assumption that there was no chemical interaction between fluoride ions and other slag constituents, the ratio k^P_{Fe} has also been calculated for these melts. Figure 11*c* shows that k^P_{Fe} values for melts containing 0·10–0·18 ionic fraction of fluoride ions are approximately one order of magnitude higher than

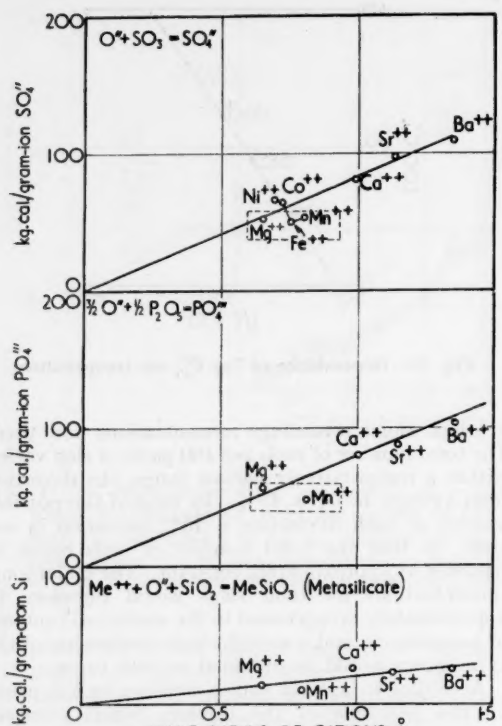


Fig. 14—Correlation between size of metallic ions and the heats of formation of complex salts from oxides

those for fluoride-free melts. This result is of considerable practical importance ; the dephosphorization of steel is greatly increased in the presence of fluoride in the slag.

Unfortunately, the small number of melts investigated by Winkler and Chipman does not allow quantitative deductions to be made on the exact effect of fluoride ions on slag–metal equilibria. Several important conclusions can be drawn, however, even from these limited data :

(1) Fluoride ions have no detectable influence on the activity of oxygen and sulphur anions ; the equilibrium ratio k_S^O is practically independent of fluoride ions (*see* Fig. 4).

(2) The effect of fluoride ions on the equilibrium ratio k_O^{Fe} is comparatively small (*see* Figs. 5 and 6). Fluoride ions increase the activity coefficient of ferrous ions, so that the equilibrium ratio $k_O^{Fe} = (Fe^{++})(O'')/[O]$ is decreased. The data in Fig. 6 suggest that the increase in the activity coefficient of Fe^{++} ions is approximately 50–100% for melts containing 0·10–0·18 ionic fraction of fluoride ion.

(3) The phosphorus equilibrium ratio increases in the presence of 0·10–0·18 (F′) to approximately 10 times the value for fluoride-free melts (*see* Fig. 11*c*). This increase would require about 250% increase in the activity coefficient of ferrous ions, if the fluoride exerted its influence on Fe^{++} ions only. As this value does not agree with that in (2), it is very probable that fluoride ions act also on phosphate ions, apparently by decreasing their activity. This effect is probably caused by chemical reaction between fluoride and phosphate ions, and as a result of strong complex formation between these ions the slag will be able to hold greater amounts of phosphorus than in the absence of fluoride ions. In view of the practical importance of spar additions in the basic open-hearth process, further detailed experimental investigation of the effects of fluoride ions is very desirable.

STABILITY OF COMPLEX ANIONS

The strong dependence of the phosphorus equilibrium ratio on the content of Ca^{++} ions suggests that the stability of the PO_4''' ion increases when Fe^{++}, Mn^{++}, and Mg^{++} ions surrounding it are gradually replaced by Ca^{++} ions. Independent confirmation of this behaviour of PO_4''' ions (as well as that of the other oxygen-bearing complex ions) is provided by thermo-chemical data. Figure 14 shows the relation between the ionic radius and the heat evolved in formation of sulphates, phosphates, and meta-silicates, per g. ion, corresponding to equations :

$$MeO + SO_3 = MeSO_4 \text{ for sulphates}$$
$$\tfrac{1}{2}(3MeO + P_2O_5) = \tfrac{1}{2}(Me_3(PO_4)_2) \text{ for phosphates}$$
$$MeO + SiO_2 = MeSiO_3 \text{ for meta-silicates.}$$

Or, in the ionic form :

$$Me^{++} + O'' + SO_3 = Me^{++} + SO_4''$$
$$\tfrac{1}{2}(3Me^{++} + 3\,O'' + P_2O_5) = \tfrac{3}{2}Me^{++} + PO_4''$$
$$Me^{++} + O'' + SiO_2 = Me^{++} + SiO_3'' \text{ (meta-silicate ion).}$$

It should be noted that the expression for the meta-silicate anion represents only the stoichiometric formula and not the actual structure, which may be formed by infinite chains or rings as shown on p. 177. The heats of formation for meta-silicates, plotted in Fig. 14, therefore refer to one g.-atom of silicon in the solid meta-silicate structure.

The heats of formation of salts with complex anions increase with increasing ionic radius of the corresponding metallic ions. The transition elements Mn, Fe, Ni, and Co show a deviation from the straight line, but the heats of salt formation of these cations are near to that of magnesium. This is of importance in the theory of phosphorus transfer from slag to metal. In regard to ionic radius r and the stabilizing effect on the PO_4''' ion, the cations normally present in basic slags can be divided into two groups :

(i) Ca^{++} ; $r = 0{\cdot}99$Å, (PO_4''' ion more stable)

(ii) Fe^{++}, Fe^{+++}, Mn^{++}, Mg^{++} ; $r = 0{\cdot}60$–$0{\cdot}80$Å (PO_4''' ion less stable).

It was found empirically that there is a linear relationship between the content of calcium ions and the sum of the group (ii) cations for basic slags saturated with magnesia (magnesia lining of the crucible and furnace in laboratory experiments of Chipman, Quarrell, and others). By extrapolation it is found that a hypothetical slag containing negligible amounts of the group (ii) cations will have 0·60 (Ca^{++}). On the other hand, the sum of cations of group (ii) will be about 0·5 when $(Ca^{++}) = 0$.

The values of the equilibrium ratio k_O^P for these two extremes can be obtained by extrapolating Fig. 11*b*.

The difference between these two values, *i.e.*,

$$\Delta k^{P}_{O} = k^{P}_{O_{(Ca^{++})=0\cdot6}} - k^{P}_{O_{(Ca^{++})=0}},$$

is related to the difference in the free energy of formation of slags containing mainly $Ca_3(PO_4)_2$ and $(Fe, Mn, Mg)_3(PO_4)_2$, respectively. The standard free energy ΔG° is correlated with the equilibrium ratio K by the equation :

$$\Delta G^\circ = -RT\log_e K = -4\cdot575\log_{10}K$$

In this case, therefore, it can be said that at 1600° C. (1873° K.) :

$$\Delta G^\circ_{(Ca^{++})=0\cdot6} - \Delta G^\circ_{(Ca^{++})=0} = -8561\left\{\log_{10}k^{P}_{O_{(Ca^{++})=0\cdot6}} - \log_{10}k^{P}_{O_{(Ca^{++})=0}}\right\}$$

From Fig. 10,

$$\log_{10}k^{P}_{O_{(Ca^{++})=0\cdot6}} = 5\cdot55$$

and

$$\log_{10}k^{P}_{O_{(Ca^{++})=0}} = 1\cdot33.$$

Substituting these values in the above expression gives :

$$\Delta G^\circ_{(Ca^{++})=0\cdot6} - \Delta G^\circ_{(Ca^{++})=0} = -36 \text{ kg.cal. per g. ion } PO_4''' \text{ formed at 1600° C.}$$

The difference in free energies of formation of calcium phosphate slags and iron, manganese, or magnesium phosphate slags, calculated in the above manner, compares well with the difference between the heats of formation per g. ion PO_4''', at 20° C., of :

(*a*) $Ca_3(PO_4)_2$ and $Mg_3(PO_4)_2$; $\Delta H = -24\cdot6$ kg.cal. per g. ion PO_4''' formed

(*b*) $Ca_3(PO_4)_2$ and $Mn_3(PO_4)_2$; $\Delta H = -33\cdot1$ kg.cal. per g. ion PO_4''' formed.

The heat of formation of iron phosphate is not known but it is probably close to those of magnesium and manganese phosphates (*cf.* the analogous case of sulphates, in Fig. 14).

These considerations may be extended to show that the replacement of calcium by strontium or barium in the basic slag should lead to a great increase of the phosphorus equilibrium ratio. The difference between the heats of formation of $Ba_3(PO_4)_2$ and $Mg_3(PO_4)_2$ ($\Delta H = -57$ kg.cal./g. ion PO_4''') is about twice as large as that between the heats of formation of $Ca_3(PO_4)_2$ and $Mg_3(PO_4)_2$. As the replacement of Mg^{++}, Fe^{++}, and Mn^{++}, by Ca^{++} leads to an increase of more than $\times 10^4$ of the phosphorus equilibrium ratio, the effect of barium ions on dephosphorization would probably be many times greater than that of calcium ions. Since the heat of formation of alkali phosphates is considerably greater than that of $Mg_3(PO_4)_2$ the presence of alkali ions should greatly increase dephosphorization by basic slags, if the slag is capable of holding alkali ions in solution. It seems, therefore, that experimental investigations on the effect of barium, and other elements in slag, on dephosphorization are highly desirable.

Increase in the stability of complex anions corresponds to a decrease of the potential energy of these atomic groupings when their environment consists of electrostatically weak cations. The structure of the slag will tend to the rearrangement that has the lowest potential energy. A preferential segregation may therefore be expected, of large cations around the complex anions and partial expulsion of smaller (electrostatically strong) cations—such as Fe^{++}, Mn^{++}, Mg^{++}—from the immediate vicinity of complex anions. The experiments of Oelsen and co-workers[20, 21] show that, when calcium or alkali ions are added to iron-oxide/iron-phosphate slags, this preferential segregation leads to the formation of two layers, one containing mainly calcium and phosphate ions and the other consisting mainly of Fe^{++} and O'' ions. In slags containing only silicate and oxygen anions, the system tends to acquire the lowest potential energy by polymerization of silicon tetrahedra, *e.g.*, by the process $2SiO_4'''' \rightarrow Si_2O_7'''' + O''$ (*see* p. 177). The tendency of phosphate ions to such polymerization is probably much smaller than that of silicate ions, and therefore the separation into two layers is preferred. The addition of sufficient amount of silica to phosphate slag closes the immiscibility gap ; thus slags containing both PO_4''' and SiO_4'''' can hold in solution high contents of ferrous ions without separating into two layers.

Figure 14 (lower diagram) shows the dependence of the heat of formation of meta-silicates on the ionic radius of the cation. The energy differences for the reactions expressed by the analytical schemes : $MnO + SiO_2 = MnSiO_3$, and $CaO + SiO_2 = CaSiO_3$, are quite small. This indicates that the replacement of Fe^{++} or Mg^{++} ions by Ca^{++} ions in acid open-hearth slags (which approximate to the meta-silicate composition) would have little effect on the principal equilibrium ratios for an acid slag–metal system (*e.g.*, $Mn + O = Mn^{++} + O''$). Experience of acid steel manufacture substantiates this conclusion.

THE EQUILIBRIUM $Fe^{++} + Mn = Fe + Mn^{++}$

The equilibrium ratio of this reaction can be expressed by the equation :

$$k^{Fe}_{Mn} = \frac{[Mn](Fe^{++})}{(Mn^{++})} \quad \ldots\ldots\ldots\ldots\ldots\ldots(30)$$

This equilibrium has already been investigated from the ionic viewpoint,[26] and it was found that the equilibrium ratio k^{Fe}_{Mn} increases with increasing contents of oxygen and calcium ions. The results of the present investigation permit more definite conclusions on the effect of oxygen and calcium ions to be drawn. Equation (30) can also be written as follows :

$$k^{Fe}_{Mn} = \frac{[Mn](Fe^{++})}{(Mn^{++})} = \frac{K^{Fe}_{Mn} f_{Mn^{++}}}{f_{Fe^{++}}} \quad \ldots\ldots\ldots\ldots(31)$$

where K^{Fe}_{Mn} is the equilibrium constant and $f_{Fe^{++}}$ and $f_{Mn^{++}}$ are the activity coefficients of ferrous and manganous ions respectively. The activity coefficient $f_{Fe^{++}}$ depends on the content of oxygen ions only (*see* equation (11), p. 175). Dividing equation (31) by $(O'')^{3/2}$ and substituting the value of $f_{Fe^{++}}$,

$$\frac{k^{Fe}_{Mn}}{(O'')^{3/2}} = \frac{[Mn](Fe^{++})}{(Mn^{++})(O'')^{3/2}} = \frac{K^{Fe}_{Mn} f_{Mn^{++}}}{K'} \quad \ldots(32)$$

Any variation of this ratio with the slag composition will thus indicate the variations in the activity coefficient of manganous ions, $f_{Mn^{++}}$. Figures 15*a* and *b* show the plot of the ratios k^{Fe}_{Mn} and $k^{Fe}_{Mn}/(O'')^{3/2}$

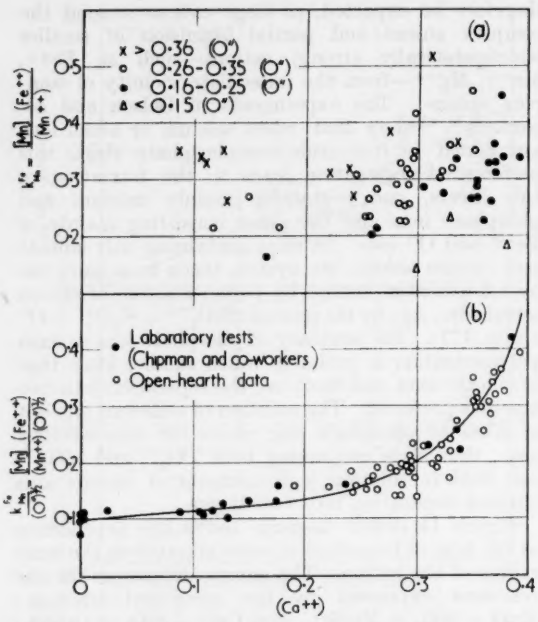


Fig. 15—(*a*) Effect of Ca++ and O″ ions on k^{Fe}_{Mn}. (*b*) Effect of (Ca++) ions on ratio $k^{Fe}_{Mn}/(O'')^{3/2}$

against the ionic fraction of Ca++ ions for laboratory melts of Chipman and co-workers, and for open-hearth tests. On eliminating the effect of oxygen ions on the activity of ferrous ions, all data fall on a single line in Fig. 15*b* ; the scatter of the points is attributed to temperature variations (which were not exactly known for the open-hearth tests) and to sampling errors.

The result is interesting in two respects :

(1) The activity of manganous ions is influenced by calcium ions ; the behaviour of Mn++ ions is thus essentially different from that of Fe++ ions.

(2) The data for open-hearth melts fall on the same curve as the data for laboratory carbon-less melts. This shows that the manganese reaction attains its equilibrium in the basic open-hearth furnace with the same ease as in the laboratory carbon-less melts, and that carbon has no effect on this reaction. From the practical point of view, the curve in Fig. 15*b* shows that at constant basicity and at constant (Fe++) content, the higher the content of calcium ions the more manganese will be reduced from the slag. Since an increase in O″ content leads to a decrease of the activity of ferrous ions, an increased basicity will also favour the reduction of manganese from slag to metal.

CONCLUSIONS

The ionic theory of slag structure outlined above permits a comparatively simple description of the principal slag–metal equilibria. The advantage of this theory is that the number of slag constituents sufficient to describe the physico-chemical behaviour of basic slags is considerably smaller than in the theories assuming the presence of oxide molecules and their compounds. Thus, according to the ionic theory oxygen atoms are assumed to be present in basic slags in only four species of particles, O″, SiO_4'''', PO_4''', AlO_3''', whereas, for example, in Schenck's theory at least 15 molecular species are assumed for oxygen-bearing compounds. The ionic theory conforms better with the physical properties of slags (such as electric conductivity, viscosity, etc.), and therefore represents a better approach to the truth.

It is difficult to say at present to what extent physico-chemical interactions between the atoms in inorganic melts and slags may be assumed to be of mainly electrostatic nature. The large variations in activity coefficients with slag composition indicate that caution is required and that the rôle of electrostatic bonding between atoms in slags must not be over-emphasized. The recent theory of valency bonding advanced by Pauling[10] may lead to a considerable modification of our views on the nature of those melts which are of interest to metallurgists.

The authors prefer, therefore, to regard the ionic theory of slag constitution as a convenient scheme which permits a more rational and simple description of equilibria than was possible by postulating the existence of discrete oxide molecules. (The latter conception has been used unchanged in metallurgical literature since the time of Berzelius.) The establishment of empirical relationships of sufficiently wide validity may be of practical interest even if their theoretical background is not fully understood.

The application of the relationships deduced in this paper to problems of steelmaking in the basic open-hearth furnace will be described in Part II, to be published at a later date.

APPENDIX

Example of the Calculation of Ionic Fractions from a Normal Slag Analysis

As stated in the text, the ions present in basic slags are Ca++, Mg++, Mn++, Fe++, Fe+++, O″, S″, SiO_4'''', PO_4''', AlO_3''', etc., and the ionic fraction is defined as the ratio of the number of g. ions, N_i, of an individual ion in 100 parts by weight of slag to the total number, N, of g. ions of *both signs* in the same amount of slag.

Some authors (*e.g.*, Temkin[27]) define the ionic fraction as the ratio of g. ions of one species to the sum of g. ions of the *same sign*. Thus two incommensurable scales of concentrations are adopted for a single melt—one for cations and another for anions. The inadequacy of this method can be demonstrated by the following example :

Let a melt consist of one mole of Na_2CO_3 and 0·1 mole of $BaCl_2$. This corresponds to :

2 g. ions of Na+
0·1 „ „ „ Ba++
1 „ „ „ CO_3''
0·2 „ „ „ Cl′.

The sum of cations $N_+ = 2·1$; the sum of anions $N_- = 1·2$. According to Temkin, the ionic fractions are :

$(Na^+) = 2/2·1 = 0·953$
$(Ba^{++}) = 0·1/2·1 = 0·047$
$(CO_3'') = 1/1·2 = 0·834$
$(Cl') = 0·2/1·2 = 0·166.$

That is, the concentration of Cl′ is seemingly 3·5

times higher than that of Ba^{++}. It would be difficult to describe some of the thermodynamic properties of melts by using two scales of concentrations for the same melt. Thus, for instance, the lowering of the freezing point of Na_2CO_3 should be proportional to the ionic fractions of ions added to Na_2CO_3, irrespective of the sign; *i.e.*, one particle of Ba^{++} should produce the same effect as one particle of Cl'. Evidently Temkin's ionic fractions will make the matter unnecessarily complex.

The method of calculation used in this paper is illustrated by the following example:

Slag Analysis, %		Gram Ions, *Ni*	Gram Ions of Oxygen from Metallic Oxides	Gram Ions of Oxygen Consumed by Anions	Ionic Fraction (*Ni*/*N*)
CaO	48·9	$N_{Ca^{++}} = 48{\cdot}9/56{\cdot}1 = 0{\cdot}8715$	$N_{Ca^{++}} = 0{\cdot}8715$		$(Ca^{++}) = 0{\cdot}415$
MgO	6·7	$N_{Mg^{++}} = 6{\cdot}7/40{\cdot}3 = 0{\cdot}1663$	$N_{Mg^{++}} = 0{\cdot}1663$		$(Mg^{++}) = 0{\cdot}079$
MnO	1·6	$N_{Mn^{++}} = 1{\cdot}6/70{\cdot}9 = 0{\cdot}0226$	$N_{Mn^{++}} = 0{\cdot}0226$		$(Mn^{++}) = 0{\cdot}011$
FeO	9·0	$N_{Fe^{++}} = 9{\cdot}0/71{\cdot}8 = 0{\cdot}1253$	$N_{Fe^{++}} = 0{\cdot}1253$		$(Fe^{++}) = 0{\cdot}060$
Fe_2O_3	3·3	$N_{Fe^{+++}} = 2 \times 3{\cdot}3/159{\cdot}7 = 0{\cdot}0413$	$\frac{3}{2}N_{Fe^{+++}} = 0{\cdot}0619$		$(Fe^{+++}) = 0{\cdot}020$
SiO_2	14·4	$N_{SiO_4''''} = 14{\cdot}4/60 = 0{\cdot}2400$		$2N_{SiO_4} = 0{\cdot}4800$	$(SiO_4'''') = 0{\cdot}114$
P_2O_5	13·3	$N_{PO_4'''} = 2 \times 13{\cdot}3/142 = 0{\cdot}1871$		$\frac{3}{2}N_{PO_4} = 0{\cdot}2806$	$(PO_4''') = 0{\cdot}089$
Al_2O_3	4·1	$N_{AlO_3'''} = 2 \times 4{\cdot}1/101{\cdot}9 = 0{\cdot}0804$		$\frac{3}{2}N_{AlO_3} = 0{\cdot}1206$	$(AlO_3''') = 0{\cdot}038$
			Total 1·2476	Total 0·8812	
			less 0·8812		
		$N_{O''} = 0{\cdot}3664$	$N_{O''\,(free)} = 0{\cdot}3664$		$(O'') = 0{\cdot}174$
		Total number of ions, $N = 2{\cdot}1009$			

References

1. H. SCHENCK : " Physical Chemistry of Steelmaking " (English Translation). London, 1945 : British Iron and Steel Research Association.
2. W. L. BRAGG ; " The Atomic Structure of Minerals." London, 1937 : Cornell University Press.
3. W. H. ZACHARIASEN : *Journal of the American Chemical Society*, 1932, vol. 54, pp. 3841–3851.
4. B. E. WARREN and A. D. LORING : *Journal of the American Ceramic Society*, 1935, vol. 18, pp. 269–276.
   B. E. WARREN and J. BISCOE : *Ibid.*, 1938, vol. 21, pp. 259–265.
5. M. A. BREDIG : *Journal of Physical Chemistry*, 1945, vol. 49, pp. 537–553.
6. J. H. HILDEBRAND and E. J. SALSTROM : *Journal of the American Chemical Society*, 1932, vol. 54, pp. 4257–4261.
7. K. ENDELL and H. HELLBRÜGGE : *Beihefte zu den Zeitschriften des Vereins deutscher Chemiker*, 1940, No. 38.
8. P. GROSS : *Zeitschrift für anorganische und allgemeine Chemie*, 1927, vol. 150, p. 339.
9. L. PAULING : " The Nature of the Chemical Bond." London, 1945 : Cornell University Press.
10. L. PAULING : *Journal of the Chemical Society*, 1948, Sept., pp. 1461–1467.
11. A. E. MARTIN and G. DERGE : *Transactions of the American Institute of Mining and Metallurgical Engineers*, 1943, vol. 154, pp. 104–114. *Metals Technology*, 1943, vol. 10, Technical Publication No. 1569, Aug., 1943.
12. J. O'M. BOCKRIS, J. A. KITCHENER, S. IGNATOWICZ, and J. W. TOMLINSON : *Discussions of the Faraday Society*, 1948, No. 4, pp. 265–281.
13. F. D. RICHARDSON : *Ibid.*, pp. 244–257.
14. E. A. GUGGENHEIM : *Ibid.*, p. 317.
15. T. B. WINKLER and J. CHIPMAN : *Transactions of the American Institute of Mining and Metallurgical Engineers*, 1946, vol. 167, pp. 111–133. *Metals Technology*, 1946, vol. 13, Technical Publication No. 1987, Apr., 1946.
16. N. J. GRANT and J. CHIPMAN : *Ibid.*, 1946, vol. 167, pp. 134–149. *Metals Technology*, 1946, vol. 13, Technical Publication No. 1988, Apr., 1946.
17. K. L. FETTERS and J. CHIPMAN : *Ibid.*, 1940, vol. 140, pp. 170–198. *Metals Technology*, 1940, vol. 7, Technical Publication No. 1164, Feb., 1940.
18. K. BALAJIVA, A. G. QUARREL, and P. VAJRAGUPTA : *Journal of The Iron and Steel Institute*, 1946, vol. 153, pp. 115–150.
19. K. BALAJIVA and P. VAJRAGUPTA : *Ibid.*, 1947, vol. 155, pp. 562–567.
20. W. OELSEN and H. MAETZ : *Mitteilungen aus dem Kaiser-Wilhelm-Institut für Eisenforschung zu Düsseldorf*, 1941, vol. 23, pp. 195–245.
21. W. OELSEN and H. WIEMER : *Ibid.*, 1942, vol. 24, pp. 167–210.
22. E. ZINTL and W. MORAWIETZ : *Zeitschrift für anorganische und allgemeine Chemie*, 1938, vol. 236, p. 385.
23. J. CHIPMAN and LO-CHING CHANG : *Journal of Metals*, 1949, vol. 1, Feb., pp. 191–197.
24. G. TAMMANN : *Archiv für das Eisenhüttenwesen*, 1931–32, vol. 5, pp. 71–74.
25. P. HERASYMENKO : *Transactions of the Faraday Society*, 1938, vol. 34, pp. 1245–1257.
26. P. HERASYMENKO : *Zeitschrift für Elektrochemie und angewandte physikalische Chemie*, 1941, vol. 47, Aug., pp. 588–594.
27. A. SAMARIN, M. TEMKIN, and L. SHVARZMAN : *Acta Physicochimica, U.R.S.S.*, 1945, vol. 20, No. 4, pp. 421–440.
28. P. T. CARTER : *Discussions of the Faraday Society*, 1948, No. 4, pp. 307–316.
29. C. R. TAYLOR and J. CHIPMAN : *Transactions of the American Institute of Mining and Metallurgical Engineers*, 1943, vol. 154, pp. 228–245. *Metals Technology*, 1942, vol. 9, Technical Publication No. 1499, Sept., 1942.
30. P. HERASYMENKO : *Discussions of the Faraday Society*, 1948, No. 4, p. 325.
31. O. ESIN : *Doklady Akademii Nauk S.S.S.R.*, 1948, vol. 59, No. 2, pp. 289–292.
32. O. ESIN and V. KOZHEUROV : *Zhurnal Prikladnoy Khimii* (*Journal of Applied Chemistry*), 1948, vol. 21, p. 765.

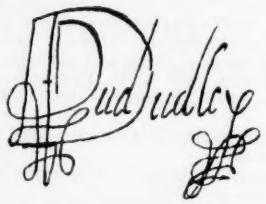
HISTORICAL NOTE No. 24

The Truth about Dud Dudley

By Dr. H. R. Schubert

DUD Dudley, the natural son of Edward, fifth Lord of Dudley, claimed to be the first to smelt iron successfully with mineral coal instead of charcoal. More than 40 years after his first attempts he set down his claims in a book which was published in 1665.[1] The book secured him a place of honour among the great inventors in history, and for the next one and a half centuries he was generally accepted as the founder of the English coal-iron industry. A more critical attitude began in 1921,[2] but despite strong criticism by noted historians of industry, such as Professor Ashton and Dr. Mott,[3] popular belief in the correctness of Dud Dudley's claims persisted, and is still persistent in history books.

Two documents recently discovered cast new light on the matter in question. One is an agreement, dated 25th May, 1618,[4] made between a London man, John Robinson of Westminster, and Edward Lord Dudley, Dud Dudley's father. The preamble refers to a patent granted to Robinson on 3rd April, 1613, for 31 years,[5] which gave him the sole privilege in England and Wales to make and refine iron and other metals with "*seacole, pitcoale, earthcoale, stonecoale, morecoale, peate, turffe, flag and brush feweel*" (*i.e.*, fuel), to build furnaces, bloomeries, fineries, and chaferies for this purpose, and to use instruments and devices which were either "*formerly used in other artes or scyences,*" or which "*John Robinson hath by himselfe or his freindes invented.*" The document goes on that Edward Lord Dudley was "*one of the principall freindes and meanes for and to the said John Robinson for the meltinge, produceinge and makeinge of iron stone or iron ewre* (*i.e.*, ore) *into sowe iron*" with mineral coal "*by a certain newe invencion and meanes which the said Lord Dudley latelye imparted and discovered*" to Robinson for the trial of which Lord Dudley "*heretofore*" spent much labour, costs, and time, and which he wanted to perfect at his own charge. For this reason, Robinson assigned to Lord Dudley the use of his patent, inasmuch as it concerned the smelting of iron with mineral coal, and it was confined to an area limited to three miles, extending from the boundaries of Dudley (Worcestershire) and Kingswinford (Staffordshire) parishes. Lord Dudley was to pay to Robinson four shillings for every ton of "*sowe iron made with the said sort of coale without some necessarie mixture of charcoale,*" and one shilling for every ton produced with mineral coal *and* charcoal. He was also to impart the complete perfection of the process to Robinson before 1st November, 1618. Within six months after this had been communicated, Robinson should have the opportunity of buying from Lord Dudley for £1000 the sole right to utilize the completed invention, either by himself or by others licensed by him. With such payment the agreement would come to an end.



Dud Dudley's signature

To sum up, the document is a contract of partnership by which a patentee (Robinson), for recompense from the profits expected, assigns the exclusive right of utilizing that part of his patent which is concerned with the smelting of iron with mineral coal, to a partner (Lord Dudley) who claims to have previously assisted the patentee in his endeavours financially and by imparting his own discoveries, and who hopes to bring the process involved to complete perfection, after which the patentee will be given the opportunity to buy the right of utilizing the so-perfected invention.

The contract implied an actual surrender of one part of Robinson's patent, for in those days when inventors had to rely on partners financing their projects, none of them would be able to pay £1000. So Lord Dudley practically secured to himself the right of smelting iron with mineral coal. This enabled

[1] Dud Dudley, "Metallum Martis: or, Iron made with pit-coale, sea-coale, etc." London, 1665.

[2] A. A. Rollason, "The Seamy Side of Dud Dudley and his Father." *The Dudley Herald*, 1921.

[3] T. S. Ashton, "Iron and Steel in the Industrial Revolution," pp. 10–12. Manchester, 1924: R. A. Mott, "Dud Dudley and the Early Coal-Iron Industry," *Transactions of the Newcomen Society*, 1936, vol. 15, p. 17 *et seq.*

[4] The document, which is preserved in the Earl of Dudley's Archives in the Dudley Central Library, was discovered by the author in March, 1950.

[5] An abstract of the patent is printed in "A Treatise of Metallica," published in 1613 and written by "John Rovinson" who is identical with the John Robinson mentioned in the Dudley document.

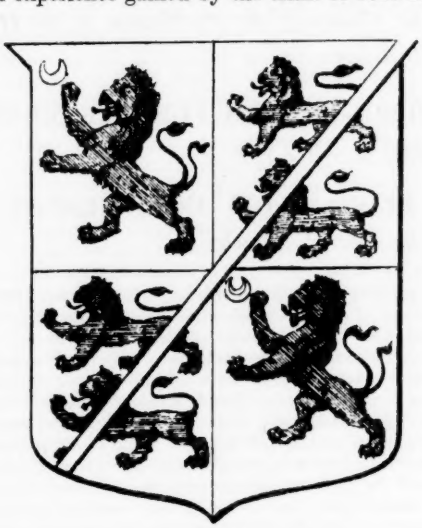
Manuscript received 11th August, 1950.

Dr. Schubert is Historical Investigator to The Iron and Steel Institute.

him to obtain a patent on 22nd February, 1622, for 14 years with the exclusive right to smelt iron with mineral coal in furnaces, and also to convert it into wrought iron.[6]

The agreement between Robinson and Lord Dudley strongly indicates that serious attempts to produce pig iron with mineral coal were made in the vicinity of Dudley before 1st November and, apparently, already before 25th May, 1618, as Lord Dudley pointed out he had spent much money and time in such trials before this date. There is, however, no record whether they had any success and practical results. The proviso that iron might be smelted with charcoal in addition to mineral coal was a safeguard which did not exactly demonstrate high hopes for complete success.

The trials took place when Dud Dudley was a youth of 18 or 19, and before he went to Oxford University. Although he never stated so in his book, he very likely had knowledge of those trials, as he refers to "*former knowledge and delight*" in his father's ironworks when he "*was but a youth.*"[7] In spite of the rather derogatory way he writes of Robinson who "*had often failed with his inventions, and great undertakings,*" it is not impossible that Dud Dudley made use of experience gained by the trials of 1618 for his



The Arms of the Dudleys

own first attempts, which he claimed to be completely successful. According to his statement they were made in 1619, when his father had recalled him from Oxford to take over the Dudley ironworks, in the Chase of Pensnett. His dating is apparently incorrect as it is inconsistent with the dates of his residence at Balliol College, Oxford, where he figures in the lists from September 1619 to about March 1622. Probably his first attempts did not take place before his father obtained a patent on 22nd February, 1622.[8]

There is not the slightest evidence on record that Dud Dudley had any success with his trials. On the contrary, his repeated assertions that he produced pig iron, castings, and malleable iron with mineral coal, in various ironworks in the vicinity of Dudley, are contradicted by a second document. This is a statement made in December 1635 by William Cope in the Court of Chancery in London, where Dud Dudley claimed the Manor of Himley in Staffordshire, and a furnace in the vicinity that he had worked for some time previously.[9] Cope's deposition is completely impartial and is imbued with full appreciation of Dud Dudley's efforts and achievements. He frankly acknowledges that the latter for several years devoted great labour and expense to the discovery of coal and ironstone mines, and also to an invention to make iron ("*hath bin for divers yeares last past at an extraordinarye great charge and trouble on the said premisses for the findinge out and discoveringe of diverse coleworkes or colemynes and of diverse ironstone mynes and hath likewise spent much labour, coste and travell in the invencion to make the said iron*").

Cope also admitted that Dud Dudley improved the ironworks so much that many tons of iron were produced. But he distinctly *denied* that Dud Dudley "*made the said iron with seacoles or pitt coles*" as the latter had alleged. This is a contemporary testimony which cuts right across Dud Dudley's claims.

Cope also refuted Dud Dudley's assertion that he had erected at great expense a furnace for smelting iron with mineral coal. This evidently refers to the erection of a furnace at Hasco Bridge between Dudley and Himley of which Dud Dudley was particularly proud because of the extraordinarily large size of furnace and bellows, which enabled him to produce per week "*the greatest quantity of Pit-cole-Iron that ever yet was made in Great-Britain.*"[10] That Cope was correct in refuting Dud Dudley's claims is confirmed by documentary evidence proving that the furnace in question existed before it was taken over by Dud Dudley.[11]

From the preceding discussion, it may safely be concluded that Dud Dudley, despite all his claims, did neither invent the method of producing iron with mineral coal, nor was he successful in any of his attempts made in various ironworks in the Dudley area. His reputation is based solely on his book, written more than 40 years after his first trials for which he claimed complete success, and written with a deliberate extolment of his merits so as to obtain an extension of his patent. He knew how to advertise, and even in those remote days it paid to advertise well.

[6] Public Record Office, Patent Rolls, C66, No. 2259, membrane 23.
[7] For this and the following compare "Metallum Martis," *loc. cit.*, pp. 3–4.
[8] Mott, *loc. cit.*, p. 23.
[9] Public Record Office, Chancery Proceedings, Charles I, D 29, No. 33.
[10] "Metallum Martis," *loc. cit.*, p. 12.
[11] Public Record Office, Chancery Proceedings, Charles I, D 42, No. 9.

DISCUSSION ON PAPERS

DISCUSSION AT MEETINGS · WRITTEN CONTRIBUTIONS

AUTUMN GENERAL MEETING, 1949

THE AUTUMN GENERAL MEETING OF THE IRON AND STEEL INSTITUTE was held on Thursday and Friday, 10th and 11th November, 1949, at the Offices of the Institute, 4 Grosvenor Gardens, London, S.W.1. The President, SIR ANDREW MCCANCE, LL.D., D.Sc., F.R.S., was in the Chair.

The Report of the Meeting was published in the August 1950 issue of the *Journal* (pp. 396–398).

Joint Discussion on the Papers—

OPEN-HEARTH FURNACE MODELS* *by J. H. Chesters, A. R. Philip, R. S. Howes, and I. M. D. Halliday*

EXPERIMENTS ON GASEOUS MIXING IN OPEN-HEARTH FURNACE MODELS† *by R. D. Collins and Miss J. D. Tyler*

and EXPERIMENTS ON THE GAS AND FLUID FLOW IN A SIDE-BLOWN CONVERTER MODEL‡ *by M. P. Newby*

Dr. **J. H. Chesters** (The United Steel Companies, Ltd.), Mr. **R. D. Collins** (British Iron and Steel Research Association), and Mr. **M. P. Newby** (British Iron and Steel Research Association), presented the respective papers. A film was shown in connection with Dr. Chesters' paper.

Mr. **L. E. Prosser** (British Hydromechanics Research Association): Although the models shown in Part I of the paper on Open-Hearth Furnace Models are intended mainly to demonstrate the important re-circulation patterns not predictable by classical hydrodynamics it is possible to derive a certain amount of quantitative information from them, particularly with regard to the minimum Reynolds number at which such model work can be carried out. The three speeds at which the tests were made correspond roughly to Reynolds numbers of 2000, 4000, and 6000–7000 at the jets, and there is evidence in Fig. 5*a* of an actual transition at the lower value, the first part of the jet being laminar. The other models, especially at the highest velocities, show a constancy of flow pattern which suggests that, above a Reynolds number of about 2000, the flow pattern does not change materially. There is some confirmation of this in some work, not yet published, which was carried out on ventilation tests for the new House of Commons by the National Physical Laboratory. Tests were made on both full-scale and quarter-scale models over a range of Reynolds numbers, and the flow patterns appeared to be the same.

I think that it would be perfectly safe, therefore, to run models of this nature at much lower Reynolds numbers than those adopted by the authors, with a consequent simplification of the technique.

In connection with buoyancy effects, I think that there is a tendency in some of the models shown—the tracer having a very much smaller density than the material, particularly when air is used—for separation to occur by centrifugal action. This, of course, is worse at the higher speeds, for although the effect of buoyancy caused by gravity is reduced, the acceleration caused by centrifugal flow is increased; and there may be danger in interpreting the models too closely with regard to the actual trace of the particles following round a curved path. There are suggestions in Fig. 3*c* and in Fig. 38 of the paper on Open Hearth-Furnace Models of some segregation of the lighter material at the centre of the vortex. This effect could be reduced if lower velocities were used in the models. The behaviour of the jets impinging at right-angles, as shown in Fig. 22 of the same paper, can be explained if it is realized that the momentum is constant in both horizontal and vertical directions. The photographs confirm that the tangent of the angle of deflection is, as nearly as can be seen, equal to the ratio of the momenta—that is to say, to the square of the issuing velocities.

* *Journal of The Iron and Steel Institute*, 1949, vol. 162 Aug., pp. 385–415.
† *Ibid.*, pp. 457–466.
‡ *Ibid.*, pp. 452–456.

Dr. **T. P. Colclough** (London) : At the Summer Meeting of the Institute at Sheffield in 1922* I demonstrated with a two-dimensional model, made of wood and glass, using water as the fluid medium, that in the flow of gases through the regenerator chambers and the furnace chamber itself, there was a main direct current and the inevitable creation of eddy flows. Since then furnaces have been watched for visual evidence of these eddy currents, which experience has shown to exist.

By using these it will be possible to anticipate many of the difficulties and overcome them before proceeding to bricks and hot gas. My impression is, however, that the authors feel that the elimination of eddy currents is a vital factor in furnace design. I am not quite so sure. There is this difficulty, which was hinted at by Dr. Chesters, that with a uniform pipe flow passing through the furnace at high speed, it may be that neither the completion of combustion nor the transfer of heat to the metal will be accomplished.

Furthermore, I have held for a long time that the eddy currents are perhaps essential for the maintenance of the furnace structure. With the intensely hot flame produced by early mixing, for which we have always striven, the radiation effect may be such that the temperature of the brickwork will come to the point of failure. I think it is possible to discern, in the results already published, evidence that the brickwork is being protected by the return eddy currents and, in particular, that the eddy currents returning to the throat of the furnace and under the roof contain very few gas products.

The main flow system is not uniform, either in the completion of combustion or in temperature. The eddy currents split off from the surface of the mass of burning gas, and this peripheral gas/air mixture will consist mainly of unused air at a temperature much lower than that of the central burning mass. This recirculating gas/air will, by virtue of its lower temperature, protect the brickwork of the furnace walls and roof, and stimulate combustion at the point where the eddy current rejoins the main central flow.

It must also be remembered that the most stable form of jet, illustrated in Fig. 6, is precisely that in which the eddy currents are most fully developed and maintain a steady direction in the main flow.

I recommend the authors to make a more intensive study of the temperature and composition of the eddy currents in the pre-combustion chamber and in the ingoing half of the furnace chamber.

It is surprising that the authors found that the removal of the wing walls made no vital difference to the general pattern of the gas flow in the semi-venturi model. The experiments showed a definite eddy system in the pre-combustion zone of the Maerz and the single-uptake designs, but in the semi-Venturi design these eddy currents are found just beyond the wing walls in the furnace chamber itself. If these wing walls are removed, why do the eddy currents enter the main stream at the same point as before, and what is the strengthening force producing this localization of the return current ?

We are all interested in the single air-port design and I suggest that one function of the wing walls at the exit end is to simulate a single port, so far as the exit from the working portion of the furnace chamber is concerned. The intense flow on both the front and back walls is also surprising, because it might have been expected that the construction at the end of the bath would correspond to a single port. The reason may be found in the large air uptakes being situated in the corner of the furnace, with the long axis in the direction of the length of the furnace.

* F. Clements, *Journal of The Iron and Steel Institute*, 1922, No. I, p. 429.

Dr. **J. S. Clarke** (Joseph Lucas (Gas Turbine Equipment), Ltd.) : Nearly 40 years have elapsed since the work of Groume-Grjimailo was first published, and there does not appear to have been much progress from the principles set out by him, except in the use of three-dimensional flow models and Reynolds criterion for dynamical similarity.

Dr. Chesters admits that he may be in trouble if he bases all his ideas of future designs on the models, because he dismisses the effect of air infiltration, which in all furnace work is of great importance. Ultimately the designer or the draughtsman has to compute areas, and he has to compute them on known coefficients of discharge. In many cases there are difficulties in calculating areas owing to air infiltration or erratic behaviour of the flow pattern. That is so in furnace design, and in the particular work with which I am connected—the design of combustion systems for gas turbines—because we find that the state of the burning flame is not homogeneous. We have carried out experiments where the flow pattern changes very abruptly, owing to changes in the flame speed in the mixture caused by the varying air/fuel ratio.

Repeatability in any experimental work with furnaces is of great importance, and it is not possible to accept the first results. I suggest that Dr. Chesters and his team should, in all their furnace work, and, in particular in all their live furnace experiments, carry out a statistical examination, because in gas-turbine work great changes in combustion often occur as the result of trifling differences.

The question of the relationship between buoyancy and dynamic head is, I think, of greater importance than the papers suggest, because of the varying temperature across the flame itself.

I was most interested to hear Mr. Prosser's comment on the Reynolds number. I can confirm what has been said in the papers and in some of the discussion. We have done this model work over a number of years, and we have produced flow patterns which are given in the paper to which Dr. Chesters refers in his bibliography. These flow patterns were obtained cold by flowing air through the combustion chamber and either injecting water or using silk tufts. In several cases we have repeated the experiment under combustion conditions by means of water-cooled yaw meters or pitôt tubes, and within the limits of experimental error the flow pattern obtained under air flow conditions has been repeated. That is the case where the Reynolds number is of the order of 700,000, compared with between 2000–3000 in the cases under discussion.

Mr. **M. W. Thring** (The British Iron and Steel Research Association) : Dr. Clarke has mentioned the work of Groume-Grjimailo. He had never heard of Reynolds numbers, and in his work, though buoyancy is simulated, turbulence is not. The tendency now is to have turbulence right and not buoyancy, but it is still hoped to develop a technique which will make both correct. That is one of the main reasons why it is necessary to observe full-size furnaces and check results of this kind.

Dr. Clarke also asked why we study aerodynamics. The first object which was clearly defined before the experiments started, was to be able to control the flame length so as to burn more fuel with a shorter flame when desired, which is largely a matter of mixing and better aerodynamics. The second object is to keep the flame off the walls when desired. The relation of the aerodynamics to heat transfer and combustion and radiation was fully recognized.

Mr. **M. P. Newby** (The British Iron and Steel Research Association) : The results of the experiments by Dr.

Chesters and his colleagues agree very closely with those which we have recently found in a trial on a cold full-scale furnace. The major forward flow of the gas occurred just above the bath, along the back wall and along the roof at the back. The rest of the chamber was filled with recirculating gases.

This result shows that scale effects are not of major importance in building models of open-hearth furnaces, and the use of relatively smooth materials such as Perspex in building these models does not appreciably affect the general flow patterns.

In regard to streamlining of furnaces, I feel that the problem of furnaces is rather different from that of aircraft. The aircraft constructor tries to eliminate turbulence, or to reduce it as far as possible, The furnace designer, on the other hand, has to produce flames which are turbulent jets. The characteristic of a jet is that it preserves its momentum until it strikes a solid object ; it then gives up its momentum in the form of pressure. The only places which might be described as streamlined are the areas where these jets impinge on the inner walls of the furnace ; here the velocities should be lowered by having the area of impact as far as possible from the point of origin of the flame, and sharp corners should be eliminated.

Mr. **I. Lubbock** (Shell Petroleum Co., Ltd.) : The most interesting feature of the work is that the flow patterns appear to tie in with the experience on the equivalent full-size furnaces, in spite of the possible criticism that the combustion process would seriously alter the pattern deduced from the equivalent flows of the fuel and air streams. Although the combustion process should produce significant changes in the pattern, it is perhaps fortunate that the authors are dealing with a furnace with comparatively low velocities and small pressure changes across the flame front.

In view of the amount of oil now used for steel melting, it is significant that no mention is made of simulating an oil-burner flame, and I should be very interested to hear the views of Dr. Chesters on how he would propose to do it. At first sight one would feel rather disconcerted in trying to simulate the scattering of oil drops, with a density about 600 times that of the air, in a model on an equivalent Reynolds-number basis, but I do not think that the difficulties are as serious as might be assumed. I should expect it to be possible to apply, as a first approximation, the authors' methods, utilizing a specially dispersed liquid nozzle equivalent to their present gas stream, on the assumption that this is the flow of the cracked and vaporized products of the oil droplets as produced in the flame front. In other words, there is no need to concentrate on the oil droplets and use pellets to get the Reynolds number ; one can concentrate on the gas which is likely to be produced from these oil droplets. In my own experience such an approximation would give valuable results, because the oil droplets do not evaporate slowly, as is sometimes stated, but evaporate and crack within periods of the order of milliseconds in the flame front.

A point of much interest in high-duty furnaces is the instability of the flow patterns with certain geometric shapes ; this is well known to furnace designers, and its effects sometimes become of great importance.

I should like to have seen more varieties of the flow-pattern in Fig. 18 with tangential jets alone, since, in the furnace with which I have to deal, and possibly in furnaces other than the open-hearth furnace in the steel industry, whirling streams and cyclone effects are deliberately introduced to get heat transference.

Dr. **A. H. Leckie** (British Iron and Steel Research Association) : In the past there has been a tendency for production managers to say that model results are of little use in full-scale practice. That is because a great deal of such work has been carried out without due regard to the laws of similarity, but it is apparent that Dr. Chesters and Mr. Newby have made a very extensive study of these laws to ensure that the limitations imposed on the experimental field by scale effects are fully appreciated.

Dr. Chesters' technique of visualizing flow deserves the highest commendation, but I would plead for further work on the iodine-thiosulphate, or similar visual-reaction technique, to which he gives brief mention, because that would give valuable information on mixing as well as on the actual flow patterns.

The magnitude of the recirculation which takes place needs closer investigation, because, if the burning gases do make several tours round the inside of the furnace before they leave, we shall have to revise our thoughts on combustion space and on the time required to transfer heat from flame to hearth. Can Dr. Chesters give us any idea of the actual proportion of the mass flow involved in this recirculation ? The impression gained seems to depend very much on the method of visualization adopted, as, for example, comparing Figs. 35 and 38.

It is a pity that there are not more diagrams like Fig. 46, for this seems to give a most convincing explanation of why roofs tend to wear in a line towards the back wall.

The vortices in Fig. 46 would forecast twin channels of wear about one-quarter and three-quarters of the way across the roof, but no doubt cold infiltrated air enters under the doors at the stage side and is carried up on the outside of the vortex so as to protect the roof towards the front lining. The only visible ' cutting ' is, therefore, towards the back wall. Would it be possible to reach a temporary solution to the problem of wear near the back lining in cases of emergency by making a few openings in the back wall along the bottom, so that cold air would be taken round to the roof above the taphole in a similar way ? We have preached so strongly against air infiltration in the past that it seems strange to say that, but it might allow an urgently needed furnace to have a little longer life in an emergency.

The technique of using CO_2 as a tracer, developed by Mr. Collins and Miss Tyler to study mixing, is capable of very wide application, and might be used even on full-scale furnaces, because the infra-red gas analyser is so sensitive that it would not be necessary to have a very large quantity of CO_2.

Do Mr. Collins and Miss Tyler consider that their mixing patterns support the wide, low gas port which, as Mr. Thring suggested some time ago, gives a flame of larger radiating surface ? It is considered that such a port, even if it could be constructed, might not be practicable because a wide flame might attack the furnace linings, but Mr. Newby's mixing patterns seem to suggest that a wide port should not cause trouble in that way.

The central air uptake design has functioned well in both investigations, and B.I.S.R.A.'s strong recommendation of this design has been based on a knowledge of this work, together with the results of the Shelton model furnace reported some time ago.*†

Dr. **H. R. Fehling** (London) : The illustrations in Part I of Dr. Chester's paper are the best means of showing that basic information on aerodynamic phenomena in furnaces can be gained only by the human eye, because these fundamental flow patterns defy purely quantitative description.

In my experience the greatest gains of model work of this kind are : (i) To make clearly visible what is some-

* A. J. Leckie and others, *Journal of The Iron and Steel Institute*, 1947, vol. 155, p. 392.

† *Ibid.*, 1948, vol. 160, p. 37.

times extremely difficult to see in an actual furnace; (ii) to train the eye to discover the same phenomena in actual furnaces once their existence has been established in the model; and (iii) to discover by model experiments how these patterns can be modified and controlled to suit the particular object, usually by comparatively small changes in the geometry of the furnace boundaries and its approach at the critical points.

Compared with these qualitative results, which are such a help to the designer and operator, the purely quantitative results, *e.g.*, data on actual flow velocities at various points, are of no more than secondary value.

There was a suspicion, at the outset, that the replacement of gas by an incompressible fluid would falsify the result, and that even the flow patterns would be different in the model and the furnace, but as long as the investigations were confined, both generally and locally, within a model to high Reynolds numbers, the inertia forces were predominant, and gravity forces (which set up purely thermal currents and displacements) were unable to change the flow pattern appreciably.

This applies to the open-hearth furnace, but it is not generally true. The best example I know is the investigation of open-furnace models by Rosin and Thring, in which no similarity of flow patterns could have been obtained by basing the model only on the Reynolds-number concept. Buoyancy effects had to be taken into account and even the process of combustion had to be imitated by dissolving salt particles. Fortunately, no such refinements are necessary for open-hearth furnace models, and I am not surprised at the conclusions that Mr. Halliday and Mr. Philip draw at the end of their paper.

It is easy to show from dimensional analysis (Part I of Dr. Chesters' paper) that these flow patterns depend on two independent groups, the Reynolds number and the ratio between nozzle area and dish area. For the same arrangement and volume flow the pattern will be affected by a variation of the jet diameter. If the diameter is very small, *i.e.*, the jet velocity is high, the jet ' penetrates ' the liquid volume ahead of it; if the diameter is large, the jet ' pushes ' rather than penetrates. Though I am sure that Dr. Chester's experiments are representative for the open-hearth furnace, this point should not be forgotten. The variations of jet velocity for constant volume flow are one of the most important methods to obtain the desired flow pattern by model experiments.

Dr. Chesters and Mr. Philip say that the fluid streams " know where they are going." I should add that they also carry with them the evidence of where they are coming from. In all similar investigations I know of, some of the most critical factors determining the flow pattern were not the geometry of the furnace itself, but the design and shape of the flues and ducts leading up to it.

In future it would pay to distinguish between true instability, *i.e.*, where no definable or no reproducible pattern can be obtained, and flow patterns which, though reproducible, are subject to fairly regular periodic changes or oscillations. These oscillations are not necessarily undesirable in practice if the frequency is not too low and the amplitude of the oscillation not too large, particularly in terms of pressure differences.

Dr. Chesters and Mr. Philip observe that the patterns are not greatly influenced by flow speed once a turbulent condition is reached. This is, as far as I am aware, generally true if stated in the form in which Mr. Newby puts it, *viz.*, that " in turbulent flow the pattern varies little within a wide range of the Reynolds number." This can be of the greatest help in model experiments if a very high Reynolds number is difficult to reproduce or leads to flow speeds which are inconvenient for observation.

Part II confirms my experience of the inadequacy of photography for record purposes. The final result should always be laid down in sketches of the type shown in Fig. 41. In this respect it would help if we could all agree on a standard method of representation.

Referring to Part III, by Mr. Halliday and Mr. Philip, I was very surprised by their results on the influence of inleakage. Because of the difficulty of reproducing this in the model, it would be valuable to hear whether observations on the furnace have confirmed what they saw in the model.

Mr. Collins and Miss Tyler could greatly add to the value of their contour pictures if in each section the boundaries between forward flow, back flow, and stagnant zones were drawn. No great accuracy would be required. Without such delimitation one may easily draw wrong conclusions, because a figure of 10% concentration has not the same practical implication in these three zones.

Mr. Newby's model work on the side-blown converter is certainly very ambitious. It is obviously impossible to obtain complete similarity in such a case. I find his results very stimulating, but his theoretical approach is not quite convincing. Wave formation on the surface of a liquid has been very closely and extensively studied in the past, owing to the general importance of the problem. This should enable us to decide which of the three properties of a liquid controls the wave formation in the present case—density, surface tension, or viscosity.

I should like to refer to the influence on model work of the combustion process itself. If this influence were confined to changes in temperature and volume I do not think that they could produce more than slight distortions of the isothermal flow pattern, unless low Reynolds numbers were being dealt with. However, combustion is a good deal more, even in the purely physical sense, than a mere change of volume and temperature. It is now certain that combustion in a flowing gas is always associated with a ' jet propulsion ' effect, *i.e.*, when the process takes place in a flowing gas its character is not purely thermal but is, to some extent, thermomechanical. A certain part of the energy released by combustion is converted into work in the direction of flow. In other words, there is not the indiscriminate expansion in all directions which has been assumed in the past.

This fact was discovered during the war in the development of flame throwers. By the use of hydrocarbon gels it is possible to prevent the atomization of the liquid fuel when squirted at high pressure through small nozzles. The jet emerges from the nozzle almost like an unbroken rod. Even so, the range of such a jet is no more than half the theoretical range of a projectile in vacuum as long as the fuel is not ignited. When ignited, and the narrow jet of liquid fuel is travelling in an envelope of enflamed vapour, this range is more than doubled, and in many cases exceeds even the theoretical range to be expected in vacuum. It was proved beyond doubt that this was not due to the effect of buoyancy. The main reason is a propulsion effect of the flame envelope on the jet it surrounds. This effect was confirmed later in ordinary gas flames where the forward momentum of the gas in the ignited zone far exceeded the value to be expected on the assumption of general thermal expansion in all directions.

I mention this briefly because it is likely that something similar may happen in open-hearth and other steel furnaces. Its effect would be to accelerate the flow of the igniting gas layers along their path, and in consequence the lateral expansion of the flame would be less

than that expected from the increase in temperature and volume. Owing to the discontinuous character of turbulent combustion, this also leads to pulsations of the flame. In small gas flames the jet actually becomes narrower, and not wider, after ignition.

Those engaged in model work on furnaces should take account of this possibility and find out by careful observation on actual furnaces whether this ' jet propulsion ' effect can be detected. Too little is known about it to make any confident predictions at present.

Regarding the question whether so-called streamline flow or turbulent flow with large back eddies is preferable, it is first of all desirable to tidy up the flow pattern in a general way. Present furnaces have been designed without the newly acquired knowledge of their aerodynamic characteristics and, therefore, flow patterns tend to be confused and unnecessarily complex. I think it is extremely doubtful whether it will be possible to generalize on the desirability of flow reversal and back eddies. In certain furnaces they greatly contribute to the stability of ignition and are, therefore, essential, but where ignition does not present any problems they may be dispensed with.

Mr. **A. Robinson** (Appleby-Frodingham Steel Co.) : The fundamental reason for these researches is to speed up the working of a steel furnace and to make its life longer, both resulting in more steel in a certain time. It has been said that the best way to speed up the working of a steel furnace is to burn more gas, but another way is to increase the radiation of the flame which is obtained. Is it possible, with a turbulent flame, to have turbulence without some eddies ? The shape of a steel furnace is almost an ellipse and, as shown by Dr. Chesters' pictures, an ellipse seems to give a very unstable pattern. That is perhaps one of the reasons why we have such a short life on many of our steel furnaces. The flame in the steel furnaces has been shown to be a series of explosions or puffs, and the question arises whether the different velocities of the flame at different times alter the flow pattern in the furnace.

Mr. **R. W. Evans** (The Steel Company of Wales, Ltd.) : I would emphasize that all this model work must eventually be transferred to the full-scale open-hearth furnace, or the work loses its value. What, therefore, are the implications of the flow patterns on the wear of the furnace and its actual working ?

When an open-hearth furnace is working on a high percentage of scrap it is often necessary to charge very quickly. This applies particularly to the ' railway ' charging system, where the scrap has to be put in quickly, and therefore is piled up in the furnace to a great extent. It seems to me that ideas on flow in the furnace may be completely wrecked if the paths which the gas has to travel in the furnace under such conditions are visualized. The Americans charge scrap at a tremendous rate and rely on the flame to break it down and make room for more. Under such conditions the eddy currents must be very strong, and the flow patterns must differ completely from those in the model.

When the scrap is right down, the hot metal has been added, and the surface of the bath—the slag surface—is plane, there is again a condition which cannot be completely simulated in a model ; the bath is then evolving gas and there must be some upward thrust of gas into the furnace atmosphere. Furthermore, if limestone is used when charging the furnace, CO_2 will be produced, and there will be a source of gas in the bath itself.

Two furnaces may seem absolutely identical in design, and yet very often, before they have had time to wear very much, they will behave in a different manner. It is difficult to explain why that should be so. It may be that one furnace is damper underneath than the other, but all kinds of other factors may arise.

After the furnace has been in operation for two or three weeks—I am speaking of double-uptake furnaces, either oil- or gas-fired—although the end of the furnace bears very little relation to the design shape the furnace still performs quite correctly. I do not know whether, having arrived at a theoretically desirable design, we shall have to water-cool the ends of our furnaces to preserve that design throughout the campaign.

Dr. **H. T. Angus** (British Cast Iron Research Association) : The early Russian work of Groume-Grjimailo was a little underestimated at the time because there were so many obvious objections to it, but an approximation with an error of 20% is better than pure guesswork. The Russian work did at least point out what many people had not appreciated before, namely, that buoyancy effects in furnace design were calculable and could be applied usefully to natural-draught low-velocity furnaces.

The term ' streamline flow ' has been used, but I do not think that streamline flow occurs in an open-hearth furnace at any point more than a foot or two from the jets, even if there. The flow of a uniform fluid is quite different from the flow of two fluids of different densities and different characteristics, and which are interacting chemically at the same time. There is no doubt that what is produced is an apparently streamlined flow of a large number of minute eddies, which must be distinguished from the main flow and the main pattern in the furnace itself. That is perfectly clear, I think, from the film which Dr. Chesters showed.

CORRESPONDENCE

Mr. **J. H. Flux** (The United Steel Companies, Ltd.) : The effect of rapidly moving metal- or slag-laden gases upon refractories has been particularly stressed by Mr. Newby, and the subject formed one of the factors considered by Dr. Chesters. This type of wear is, of course, common to both the open-hearth furnace and the converter, and as the cause of the action is almost identical in both cases, any information gained from the study of models of one type can generally be applied to the problem as it affects the other type of furnace. The results mentioned in both papers support the view that maximum erosion occurs in zones of highest gas velocity. It is imperative to be able to plot the flow pattern of the gases, but it is also essential to try to measure the rates of wear, and to indicate the proportion of the wear caused by : (*a*) The action of the gases passing over the refractory ; and (*b*) the impingement upon the lining of particles of solid matter thrown out of the turbulently flowing gas streams.

The water-model technique gives an excellent indication of the flow pattern and of the relative order of the gas velocities, but it does not assist in proportioning the amount of wear from the differing causes. Would Mr. Newby, in a work specifically undertaken to determine the causes of wear, have obtained much more useful information by the use of an air model ? By using this type of model smoke could have been introduced into the air to give the flow pattern, and small particles could have been injected to assimilate the effect of the gas ' picking up ' either slag and/or metal.

At the moment, the model work by Mr. Newby gives an indication of the flow pattern which is very complex, and although calculations for the behaviour of solid matter in cyclones are well known, it would be exceedingly difficult to adapt these calculations to the totally different case of the converter. After the flow pattern in the port and down-takes of an open-hearth furnace

had been obtained by Dr. Chesters from a two-dimensional water model, as shown in the film, it was found possible to develop calculations to determine the path of solid matter carried by the gases leaving the furnace. These calculations have shown remarkable similarity between the calculated and actual positions of seriously eroded areas of refractories in the down-take and in the position of the slag deposits in the pockets of one particular furnace. It now remains for the work to receive the double check provided by an air model, and it would be of assistance to know whether Mr. Newby had considered any such approach to his problem.

Mr. **D. J. O. Brandt** (British Iron and Steel Research Association) wrote: I consider that Mr. Newby's conclusions on the experiments with the side-blown (Tropenas) model should not go entirely unchallenged, as there is reason to believe that there may be another factor which is not allowed for in the model.

Mr. Newby has been particularly concerned to provide an explanation of the wear on a converter lining around the tuyeres which, as has been well illustrated already,* is the most serious aspect of refractory corrosion in side-blown practice. Compared with the rate of wear at the tuyeres, the rate of erosion at the point immediately opposite the tuyeres is a very minor affair, and certainly not one of the converter operator's main problems.

In Mr. Newby's model converter, the existence of a backward gas eddy sweeping over the lining of the converter above the tuyeres has been demonstrated, particularly in the short film which was exhibited. This film also showed that while the tuyere area was being subjected to a gentle 'raining' action of the eddying gas the wall opposite the tuyeres was undergoing something more in the nature of a massed attack with fire-hoses! Mr. Newby admits that the velocity of the eddy in the tuyere area is only $\frac{1}{10}$ of that of the gas striking the front wall, but he considers that the conditions of this eddy are such as to enable it to erode the refractories considerably faster than the stream of air which comes out of the tuyeres, passes across the surface of the bath (presumably becoming highly charged with FeO in the process), and then strikes directly against the opposite wall at a velocity ten times as great.

Because of the experience gained with air and oxygen lances in open-hearth practice, and the damage which these relatively small gas streams can sometimes do to the open-hearth roof, I submit that if Mr. Newby's model truly represented all the conditions inside a full-scale Tropenas converter in regular use, then the operator would find a large hole in the side of his vessel opposite the tuyeres, long before these items were ever due for renewal.

I consider that the factor not taken into account in the model is the possible change in the level of the metal surface in a converter when the blast is turned on and the very rapid conversion reactions take place. If a Tropenas converter blow is complete in approximately 15 min. with an initial carbon content of 3%, then the bath 'boils' at the rate of 1200 'points' of carbon per hour (one point = 0·01% C). A good open-hearth boil may give a carbon elimination of roughly 30 points/hr., so the converter boil is some 40 times more rapid. It is well known that during the open-hearth boil the general level of the bath may rise appreciably, owing to the evolution of the gas from the metal and the entrainment of gas bubbles in the slag. (The water in a common domestic kettle rises in a similar way when boiling commences.) For a side-blown converter to function properly, the surface of the bath before blowing must reach up to the lip of the tuyeres, and it is surely reasonable to argue that a boil of 40 times the intensity of that in an open hearth, taking place in a relatively much deeper and narrower vessel, may be more than sufficient to raise the bath level to such an extent as to effectively immerse the bottom ends of the tuyeres when the action is under way.

I submit, therefore, that the 'action' of Mr. Newby's model converter is an incomplete picture of the real thing. In actual practice the ends of the tuyeres are immersed, and the rapid erosion which takes place here is the same type of erosion which progressively destroys the tuyeres in the bottom-blown converter. The air stream does not sweep across the metal surface at all, but bubbles obliquely into the boiling melt, generating a zone of intense temperature and agitation in which an intensely hot metal-surface concentrates heat on to the tuyere zone. Thus, the front wall of the converter is far more dangerously exposed than the back wall, and therefore erodes much faster.

My argument thus confirms Mr. Newby's proposal to proceed with the completion of a periscope to observe the interior of an actual full-sized converter in operation. The open-hearth model experimenters are less exposed to pitfalls of this kind, since they have only to open a furnace door to satisfy themselves that conditions (apart from Reynolds similarity, etc.) in their models reasonably approximate those of the shop. In the side-blown converter this is much more difficult, and the factors that I have mentioned may well change the picture entirely. Because much of the erosion in an open-hearth furnace can be accurately traced to the action of dust-laden furnace gases, Mr. Newby has assumed that the refractory wear in the side-blown converter must be similarly caused. This initial premise may well be incorrect, and I would urge that this point should be cleared up as soon as possible.

*First Report of the Converter Refractories Sub-Committee, *Journal of The Iron and Steel Institute*, 1947, vol. 155, p. 240.

AUTHORS' REPLY

Dr. **J. H. Chesters,** Mr. **A. R. Philip,** Mr. **R. S. Howes,** and Mr. **I. M. D. Halliday** wrote in reply: The contribution by Dr. Colclough is extremely interesting and useful, but we are inclined to think that eddy currents are, on the whole, unfavourable to refractories. The principal objection is that return flow from the region of the bath inevitably brings with it large quantities of iron oxide and other fluxes, which, when brought into contact with the roof, result in rapid wear. If the layer beneath the roof was clean air it would offer protection, but gas analyses, *e.g.*, those given in *Special Report No.* 37,* show that even under the Venturi roof there is an average CO_2 content of 8%, suggesting that at least half of the gases here consist of products of combustion. Furthermore, the temperature of these gases is likely to be at least as high as that of the roof, since they come in such large measure from the flame itself.

The small change in flow pattern with the removal of the wing walls in the semi-Venturi design was a surprise to us also. It would appear that the verb or slope of the ramp roof has a more vital effect on the flow, but it is possible that, in the Venturi furnace as originally designed, the effect of removing the wing walls might be appreciably greater.

In reply to Dr. Clarke we can only repeat that the fuel velocities at entry, even for a gas-fired furnace, are very high compared with those likely to occur because of buoyancy, and that the amount of lift in a hot furnace is small even in a central position. The lack of any

* *The Iron and Steel Institute*, 1946, *Special Report No.* 37, p. 142.

serious buoyancy effect is confirmed by the fact that cinematograph pictures of flames at the furnace doors show only slightly higher levels than those observed in the water model. The relatively slow entry of air through doors, and its dominance by the major flow pattern in the furnace, has since been confirmed by observations on actual furnaces.

The answer to Mr. Lubbock's question is that we decided to compare the results reported on Templeborough furnaces in *Special Report No.* 37 with those on the corresponding models, and at the time of the Templeborough trials there were no oil-fired furnaces there. Since the present paper was published we have made a considerable number of trials both on actual oil-fired furnaces and on models of them. We hope to publish some of our results soon. In the meantime we may say that the problem of attaining similarity is far more complicated than with a gas flame.

We cannot give a definite reply to Dr. Leckie's question about the proportion of the gases actually recirculating, but we imagine that if a furnace was sectioned through, say, the first door, at least 20% of the flow would be found to be in a reverse direction. We believe that furnaces could be designed in which the return flow was virtually eliminated, or alternatively, in which it was very markedly increased. We do not consider that the making of holes in the back and front walls, to enable air to be entrained by the gases as they pass up the walls and thus reduce the wear on the roof, would be a good idea, since it would undoubtedly reduce the overall fuel efficiency. Given the right flow pattern, we believe that it will be possible to burn larger amounts of oil and yet run with a markedly cooler and cleaner roof than we are able to at present.

Dr. Fehling spoke of the need for a set of flow pattern symbols. We are using such a set ourselves, but we hesitate to recommend it as we find extreme difficulty in portraying three-dimensional flow on a two-dimensional sheet of paper. For example, in attempting to describe the flow in a cone we have resorted to preparing a wire model and having a sketch drawn of this for subsequent reproduction. The problem will have to be tackled, since studies on actual furnaces do not enable one to portray the flow in a series of horizontal and vertical planes in quite the same manner adopted for water models.

In regard to the question on whether the results of model work are corroborated in practice, we can only state that we have made a number of cross-checks and found the major features to be extraordinarily similar.*

Mr. Evans' point about scrap is extremely important. Virtually all the work on models, both in our laboratories and elsewhere, has ignored the scrap pile and assumed the flat-melted condition. Since there is no particular difficulty in maintaining temperature once the furnace is flat-melted and increased heat release rates are mainly desired during the melting-down period, it is vital to consider what effect the scrap pile has on the shape of the combustion chamber. We have recently obtained precise data on typical scrap-pile shapes, and, in future, will simulate these in both the water-model and the hot-model work. We have already found examples of designs that would be quite satisfactory in the absence of scrap, but almost inoperable when a scrap pile is present.

We do not consider evolution of gases from the bath to be a major effect, except during certain special periods in hot-metal practice. It is doubtful whether it will require any more attention from the furnace design aspect than, say, the comparable problem of air infiltration.

Dr. Angus has entered an extremely controversial field by referring to streamline flow. We like to visualize the motion within the moving gases as divided into three sections : (1) Molecular diffusion ; (2) micro-turbulence ; and (3) macro-turbulence. When we speak of ' flow pattern ' it is item (3), *i.e.*, the large eddies, to which we are referring, but within, say, the flame itself all three forms of motion are present. Because aluminium particles in the main jet of a water model show parallel streaks, this does not mean that the flow is non-turbulent, but merely that these large tracer particles have a forward motion, which is very rapid compared with any sideways motion caused by micro-turbulence. That the latter exists is clearly shown by the impossibility of getting satisfactory patterns at these high Reynolds' numbers by employing dyes. The small particle size here results in rapid sideways spread, and no clear idea of flow pattern is obtained.

Mr. **R. D. Collins** and Miss **J. D. Tyler** wrote in reply : Mr. Prosser's suggestion that furnace models could safely be run at considerably lower flow rates than those demanded by Reynolds similarity is supported by a test made by us on the semi-Venturi model, in which a reduction of more than 2 : 1 showed no significant change in the mixing contours. The purpose of the test was to ensure that the results obtained were not only applicable to a narrow range of Reynolds numbers, for if they were, a change of preheat temperature or flow rate would alter the mixing pattern of a furnace. In this case the mixing diagrams would be of little use.

Dr. Colclough asks whether back flow of gases in a furnace protects the refractory. Mixing experiments provide no direct evidence of refractory life, which may explain the somewhat surprising result that from a mixing standpoint the simpler Maerz design proved better than the semi-Venturi. The result was surprising because, if mixing were the only criterion of design, a knuckle would appear to be a useless complication. In fact, refractory life is as important as combustion efficiency, and mixing experiments by themselves provide no evidence of that.

The low wide gas port appears to provide quicker mixing, providing that there is adequate access of air around the perimeter of the gas. It is, therefore, very suitable for use with the single air uptake, but in other designs, if the lower surface is blanketed by the hearth, its advantages are lost.

Mr. **M. P. Newby** wrote in reply : Mr. Prosser spoke of the possibility of errors in flow visualization because of the centrifugal forces acting on bubbles in a flowing liquid. In the work on the side-blown-converter model this effect was considered to be negligible. Normally the Reynolds number in the body of the converter was of the order of 16,000. If this was reduced to about 1000, when the flow was near the transition region to streamline flow but was still just turbulent, the pattern traced out by the bubbles was found to be the same.

In regard to Dr. Fehling's point about waves on the surface of steel in a converter, it seems unlikely that a regular wave pattern establishes itself. The low kinematic viscosity of steel and the size of a converter will ensure that viscosity will not have much effect on metal surface disturbance. The viscosity of the slag will be very much higher, but its volume will be small.

Mr. Flux asked whether it would not have been better to build an air model and inject solid particles to simulate the effect of particles of slag and metal in the study of erosion in converters.

The conditions of particle size and density would be difficult to simulate until we have a good idea of what

* Examples of these checks will be given in a paper to be included in the Symposium on Flow arranged by the Institute of Physics for October 1950.

happens in an operating converter. However, we have carried out some simple experiments with dust particles suspended in the blast, and collected them on the inner wall of the model by making it sticky. The result showed that the greatest amount of material was deposited on the front wall, but that the highest concentrations on the back wall occurred between the tuyeres.

As the deposition of particles is intimately connected with flow pattern we considered it better to determine this first, because of the easier conditions of similarity.

I should like to say a little more on the subject of erosion, which I feel has not been brought forward as much as it deserved during the discussion. One of the principal uses of this model work on furnaces is the relationship which it seems to bring out between flow pattern and erosion of refractories. The work by Dr. Chesters' team and our own work on a full-scale furnace passing cold air show that the heavy erosion occurs in the region where the gases, rising up the back wall, impact on the roof. This region of the back of the roof is one where the moving gases not only have to change direction abruptly, but where they also have high velocities. If the suspended material, which will be flung on to the roof, consists of slag picked up from the bath, it will cause heavy localized erosion. This erosion is often more severe in oil-fired furnaces, and we attribute this to the higher velocity of the gases just above the bath ; the pick-up of slag particles, therefore, is likely to be greater.

A model of an oil-fired furnace can be built, using an air jet, if it is remembered that the momentum of a jet is proportional to the squares of the kinematic viscosity and the Reynolds number, and directly proportional to the density. It has to be assumed here, however, that the evaporating of the oil droplets does not have much effect upon the greater part of the flame.

The points raised by Mr. Brandt had not been overlooked during the course of the experiment. The possibility of a boil modifying the conditions considerably has always been admitted. For example, Fig. 4 shows the appearance of the bath when an artificial boil was induced. A considerable amount of liquid is thrown up inside the converter and some of it leaves through the converter nose, but the blast still appears strong enough to keep the metal back from the tuyeres. What would be expected to occur if the tuyeres were submerged is shown in Figs. 3*a*, *b*, and *c*.

The deposition of particles from a stream is a function of the centrifugal forces acting on them, and this depends not only upon velocity but also upon the radius of curvature of the path.

There is no doubt that the recirculating gases in the model suffer a very sharp change of direction close to the tuyeres, and any suspended material will be deposited much more easily on the tuyeres than on any other region of the back wall. This has been shown by the use of dust, which was deposited on the back wall most thickly between the tuyere holes.

Although the velocities on the front wall are higher than those on the greater part of the back wall, the velocities in the tuyeres are much higher still, and the greatest drag forces will exist there. Therefore, these two effects of sharp curvature and high velocity at the tuyeres may account for their high erosion rate. Until the bath condition has been observed it will not be possible to decide what mechanism is responsible for the wear, and we hope that the completion of an optical apparatus for doing this will enable the question to be settled in the near future.

In conclusion I should like to make a correction to the formulae published in my paper. The Reynolds numbers should be :

$$\frac{V_G l}{\nu_G} \text{ and } \frac{V_L l}{\nu_L}$$

Discussion on the Paper—

MECHANICAL PROPERTIES OF LOW-CARBON, LOW-ALLOY STEELS CONTAINING BORON* *by W. E. Bardgett and L. Reeve*

Mr. **W. E. Bardgett** (The United Steel Companies, Ltd.), presented Part I of the paper and added : The effect of boron in the presence of chromium was investigated for only one chromium steel, which contained 0·57% of Cr (Series VIII). Tests have been extended to cover chromium contents up to 1·50%. The analyses and test results are given in Table A, Series XVII being plain chromium steels and Series XVIII corresponding steels containing boron. The steels were all tested in the form of $\frac{5}{8}$-in. dia. bar in the normalized condition.

Comparing the two series and allowing for the differences in carbon and manganese contents, the effect of boron on the maximum stress is negligible, but there appears to be a very slight beneficial effect on the yield stress. The effect of boron on the ductility and toughness appears to be quite definite, the effect being beneficial at the high chromium contents, particularly with respect to toughness.

In several of the series of steels given in the paper the effect has been shown of varying molybdenum content in the presence of boron after the important and, in some cases, critical nature of the molybdenum content had been determined. To obtain a measure of the influence of boron in a series of steels of varying molybdenum content, further tests were carried out on Series XIX of 1% Cr–Mo steels treated with synthetic Silcaz without boron (Table A) for comparison with the corresponding Series XVI containing boron added as Silcaz. With molybdenum contents up to approximately 0·20%, boron has no definite effect on the mechanical properties, but at 0·30% and above, the maximum stress and yield stress are markedly increased, and the elongation and izod impact values are correspondingly reduced, but the reduction of area values show a distinct increase.

Dr. **L. Reeve** (Appleby-Frodingham Steel Co.) presented Part II of the paper.

Dr. **N. P. Allen** (National Physical Laboratory) : The search for an easily weldable plate steel having a yield-point above 30 tons/sq. in. and good bending and impact properties has occupied steelmakers for many years. It is possible to doubt whether the authors have yet reached their objective entirely, but they have written a most interesting and stimulating paper.

Properties such as have been described can be attained, or approximated, in a variety of ways. The use of molybdenum seems to be common to them all, but whether there is anything peculiar about the use of boron or whether this is just another manifestation of the well-known effect of boron on hardenability is questionable.

* *Journal of The Iron and Steel Institute*, 1949, vol. 163, Nov., pp. 277–294.

As either the rate of cooling or the hardenability of a steel of this kind is raised, the yield point first increases in a fairly gradual manner, and then more suddenly. The sudden rise may or may not be accompanied by a startling decrease of ductility. The higher values of yield point in normalized plate steels do not seem to be obtainable by molybdenum alone, but the addition of something else besides molybdenum is required which will increase the hardenability to the extent needed.

It seems that additions of nickel, carbon, manganese, chromium, or boron are required. Carbon helps, but it is important to note that if high ductility and impact resistance are required after the improvement of yield point has taken place it is desirable for the carbon to be below 0·20%. The paper shows the desirability of a low carbon content, and that remarkably high yield points can still be achieved with a carbon content as low as 0·05%.

The addition of chromium also appears to be accompanied by brittleness in the conditions of raised yield strength, and brittleness also results if too much boron is added. In obtaining these desirable properties, therefore, conditions are very delicately balanced, and the element of control is accordingly very important.

I imagine that, in obtaining these properties, one is suppressing the separation of the coarse ferrite and the pearlite associated with the pearlitic transformation, and replacing it by acicular ferrite and bainite constituents which are characteristic of the intermediate transformation. For this reason, elements which have a very vigorous influence on the intermediate reaction, and therefore suppress the formation of the bainitic products, are to be avoided.

It is interesting to speculate on the causes of the very high yield point. Recent work* suggests that when acicular ferrite is formed at relatively low temperature it may contain a significant amount of carbon in solid solution. Whether this has any bearing on the value of the yield point is more than can be said at present, but it may suggest a reason for the disappointingly low impact values of the thicker plates, particularly in the rolled condition.

Finally, it is to be noted that the future of a steel of this kind depends largely on the cost. The fact that boron is effective only in a fully killed steel, of which the yield will be low, is a disadvantage. Certainty in obtaining the desired products with sufficient latitude to provide for the inevitable accidents of production is also an important factor, and in this connection it is pleasing to see the close control which the authors have succeeded in maintaining over the boron contents of the steel.

Dr. **H. A. Dickie** (Messrs. Stewarts and Lloyds, Ltd.) : Until recently the element boron has been little used in ferrous metallurgy. Its principal use has been in America, where it has been used, or its use has been suggested, as a depth hardener in medium-carbon and alloy steels, with the object of saving strategical alloys during the war. The capacity of boron for increasing the depth hardening of steels appears to be established, especially since its effects can only be made evident by the protection of aluminium additions which would normally decrease the hardenability. The new application of boron proposed by the authors can logically be regarded as an extension of previously established effects.

The effect of boron in promoting greater depth hardening depends on the alteration which it makes to the critical cooling speed, which in turn presumably depends on the distortion produced in the γ-iron lattice. It is quite natural that it could also be applied to lower-carbon steels to alter the critical cooling speeds, since these affect not only the hardenability but also the general properties of steels in the non-hardened condition, as may be exemplified by many known effects of other alloy additions in ferrous metallurgy.

It is also not surprising that only very small amounts of boron are needed to produce powerful effects. In fact, this is a general characteristic of elements which have a limited solid solubility in iron. For example, hydrogen, nitrogen, and carbon in α iron have this characteristic. Very small atomic percentages of these elements, of the same order as the small amount used in the case of boron, can produce equally remarkable, but not necessarily identical, effects. These elements are interstitially dissolved in the iron, and the limit of solid solubility is of the same order as that of boron. There is also the element copper, which dissolves substitutionally and is of limited solubility, but not so limited as in these other cases. Copper, too, can produce large-scale effects on the mechanical properties. All these effects are

* J. Trotter, D. McLean, and C. J. B. Clews, *The Institute of Metals*, 1949, Monograph and Report Series No. 8, p. 75.

Table A

ANALYSES AND MECHANICAL PROPERTIES

Steel	Analyses					Boron, %		Heat-Treatment	Mechanical Properties				
	C, %	Mn, %	Si, %	Cr, %	Mo, %	Sol.	Insol.		Max. Stress, tons/sq. in.	Yield Stress, tons/sq. in.	Elong. on 2 in., %	Red. in Area, %	Izod, ft. lb.
Series XVII : Low-Carbon Cr Steel. Variable Chromium Content													
117	0·12	0·40	0·34	0·47	..	..	..	950° C., A.C.	30·0	20·1	41·5	71·0	101
118	0·12	0·38	0·30	0·77	..	..	..	,,	31·1	20·8	42·0	72·5	100
119	0·14	0·46	0·35	1·01	..	..	..	,,	33·7	21·3	36·5	72·5	87
120	0·14	0·47	0·36	1·29	..	..	..	,,	37·7	21·2	31·8	63·5	73
121	0·14	0·38	0·30	1·55	..	..	..		36·0	20·7	33·5	63·0	49
Series XVIII : Low-Carbon Cr–B Steel. Variable Chromium Content													
122	0·15	0·58	0·45	0·55	..	0·0026	0·0012	915° C., A.C.	32·5	21·9	41·0	73·0	79
123	0·14	0·64	0·47	0·80	..	0·0022	0·0015	880° C., A.C.	34·3	22·3	39·0	72·5	75
124	0·15	0·61	0·45	1·05	..	0·0023	0·0020	885° C., A.C.	34·8	23·3	39·0	73·3	90
125	0·15	0·63	0·46	1·30	..	0·0021	0·0017	890° C., A.C.	36·0	23·5	38·0	72·5	89
126	0·15	0·46	0·47	1·75	..	0·0015	0·0028	905° C., A.C.	37·1	24·5	38·0	72·5	95
Series XIX : 1% Cr–Mo Steel. Variable Molybdenum Content													
127	0·12	0·53	0·46	1·09	0·10	..	..	955° C., A.C.	34·6	23·7	41·0	75·7	99
128	0·13	0·58	0·46	1·10	0·21	..	..	,,	40·8	25·5	30·0	53·3	37
129	0·14	0·54	0·43	1·10	0·29	..	..	,,	44·2	26·9	28·0	50·5	33
130	0·15	0·56	0·43	1·09	0·42	..	..	,,	46·8	29·9	29·0	46·7	31
131	0·14	0·54	0·42	1·09	0·52	..	..	,,	46·8	26·5	23·0	27·0	38

presumably due to the distortion of the γ-iron lattice.

This paper was published only recently, and it may be that there is little in the way of existing data from other sources with which the authors' conclusions may be checked. It happened, however, that we had from one of the authors, a short while ago, an account of this projected development and, as it appeared possible that we might at some time desire to treat our own steel by these methods, we made, unknown to the authors, a small cast as an independent check. This was an induction-furnace cast, weighing 20 lb., of molybdenum steel, treated in the way which we understood was advised by the authors, taking care to make the aluminium additions before adding the boron, and finally cooling the steel from the normalizing temperature at what we believed was the prescribed cooling rate. The properties of this cast were no different from the properties of the same composition of steel without boron.

We then made something like 15 casts of molybdenum steel and chrome–molybdenum steel, using in some cases ferro-boron and in others Silcaz. None of these casts produced the results which we understood that the authors produced; there was no difference in the mechanical properties from the same compositions of steel without the boron.

We suspected some difference in minor constituents in the steel. Our steels had been made, using as a base metal, basic Bessemer steel scrap, which, as is generally known, is unusually pure and very low in generally unwanted impurities such as nickel and copper. A further cast was made, therefore, to which was added 0·25% of nickel and 0·25% of copper, everything else remaining the same as before; and, at last, the authors' results were reproduced. The tensile strength was raised, for example, from between 26 and 30 tons/sq. in. to 39 tons/sq. in., and the yield point from about 17 tons to about 28 tons. Further casts were made, to which nickel alone and copper alone were added—0·25% in each case—and both these compositions gave the enhanced properties described by the authors.

The molybdenum content was then increased. In the earlier casts it had generally been between 0·35% and 0·38%, but in one case it was 0·47%, which, when increased to 0·55%, reproduced the effects in the steel with the pure base.

On seeing the authors' full figures for the first time, I examined their compositions, and as far as I can see, they used generally a steel with quite a pure base. Nevertheless, the lowest copper content recorded in their paper is 0·06%, except in one case, where it is 0·045% in the presence of 0·1% of phosphorus. The copper content of our steels was about 0·015%. These may seem very small differences to account for the variance between our experience and that of the authors, and it may be that other elements, not already mentioned, are the cause. In any case, we are considering a kind of homeopathic procedure, in which very small doses may, if properly administered, produce remarkable results.

There has not been a great deal of time in which to formulate this contribution, nor to review the results, with an additional result every half hour or so which slightly alters the picture, but I imagine from the results which we have obtained that the authors would encounter some surprises and disappointments where the base metal was particularly pure, and with the warning which I am giving them now, they will have a good chance of offsetting the disadvantage of too pure a base by ensuring that they make it impure or else by adding sufficient molybdenum.

There are one or two points of detail on the paper to which I should like to refer. Almost all the casts that we made should have given the results intended, according to Fig. 14; that is to say, in the great majority of cases we had more soluble boron present in the cast than the authors gave as the amount necessary to produce the effects. I can at present only accept the conclusions in Fig. 14 as referring to a particular set of circumstances, and I do not accept them as of general validity. I am not a chemist, but I believe that boron oxide, B_2O_3, is soluble in acid, and that at least one of the boron nitrides is soluble in acid. At the moment I would not accept the soluble portions of boron in the analysis—*i.e.*, the boron which goes into solution in acid when the steel is dissolved—as representing the boron that is present in solid solution in the steel.

Monsieur **A. Kohn** (Institut de Recherches de la Sidérurgie, St. Germain): In France, the Institut de Recherches de la Sidérurgie has also engaged in a study on boron steels, and many tests were carried out with the co-operation of three industrial laboratories. The first work was concerned only with medium-carbon steels.* Small ingots had been cast from high-frequency furnaces at Aciéries d'Ugine and Etablissements Schneider; at Anciens Etablissements Cail, one cast of six 1000-lb. ingots was made in a 5-ton basic electric furnace. Boron was incorporated in the casts as ferro-boron, its content extending from 0·001 to 0·016%. The six 1000-lb. ingots were forged into 1-in., 2-in., 4-in., and 8-in. dia. bars, which were tested after normalization or quenching and tempering.

Ferro-boron additions can have two principal effects: (i) They increase the austenitic grain size at the austenizing temperature; and (ii) they remove the **S**-curve to the right.

Boron greatly increased the maximum stress and the yield stress of the 1-in. dia. water-quenched bars; by such cooling conditions a martensitic structure is formed in boron steels, whereas there is only troostite and ferrite in steels without boron. But in all other cases (8-in., 4-in., and 2-in. water-quenched rounds or oil-quenched and normalized bars) the effect of boron was of little importance, or was detrimental if a large grain size had a predominating harmful action (centre of the 8-in. and 4-in. normalized rounds).

The authors tell us that boron additions made to 0·5% molybdenum steels lower the temperatures where the pearlite formation is taking place, if the steels are cooled with higher velocities than the "limiting rate of cooling"; under these conditions, the maximum stress and the yield stress are increased. We think that boron has the same effect upon these normalized molybdenum steels as upon the water-quenched medium-carbon steels which we studied. Boron delays the austenitic decomposition in isothermal conditions. During continuous cooling with a proper mean velocity, the transformation occurs in a lower temperature range, so that the final constituents are harder (martensite in quenched medium-carbon, and fine pearlite and acicular ferrite in normalized molybdenum steels). If cooling is too slow, boron is ineffective and there is no increase of maximum stress. In this respect we cannot compare boron to such alloying elements as nickel or chromium, which change the mechanical properties of steel whatever the thermal treatment may be.

The purpose for which our tests were carried out was not the same as the authors'. Nevertheless, our conclusions correspond fairly well with their own results upon one important point, namely, that there is a definite relation between the efficiency of boron addition

* A. Kohn, *Revue de Métallurgie*, 1949, vol. 46, Dec., pp. 859–871; *Ibid.*, 1950, vol. 47, Jan., pp. 55–87.

Table B

NON-METALLIC RESIDUES EXTRACTED BY THE DICKENSON METHOD

Composition : 0·35–0·40% C, 1·0% Mn, 0·25% Mo

Samples	Ferro-Boron		Silcaz	
	5045 (0·003% B)	5050 (0·018% B)	5146 (0·004% B)	5147 (0·010% B)
	***Ignited Residue*, %**			
SiO_2	0·001	0·001	0·092	0·008
Fe_2O_3	0·002	0·002	0·002	0·001
Al_2O_3	0·020	0·028	0·015	0·004
MnO	nil	nil	nil	nil
TiO_2	nil	nil	0·001	0·016
ZrO_2	nil	nil	0·048	0·034
	***Dried Residue*, %**			
B	0·0011	0·0015	nil	nil
N	0·0013	0·0019	0·002	0·0013

Note : Ratio $\frac{B}{N}$ 46·5/53·5 — Boron Nitride 45·0/53·0 — 43·5/56·5

and the soluble acid-boron content, as determined by Rudolph and Flickinger's method. We observed that small boron additions (less than 0·008%) were ineffective on our steels. As in the authors' work, boron additions were proved effective only when the acid-soluble boron content was more than approximately 0·0010%. The nitrogen content of these steels was high (more than 0·010%), and we found that the soluble acid nitrogen was increasing when the total boron amount was increasing. Digges and Reinhart* also indicate that low ferro-boron additions without titanium are ineffective in high-nitrogen-bearing steels. We suppose, therefore, that boron may enter into combination with nitrogen and is ineffective in this form. All these results confirm that it is necessary to fix nitrogen by titanium as a stable nitride. We hope that by further tests we shall be able to make the effect of nitrogen more precise.

* T. G. Digges and F. M. Reinhart, *Transactions of the American Society for Metals*, 1948, vol. 40, pp. 1124–1146.

Mr. G. E. Speight (The United Steel Companies, Ltd.) : We also have some views on the modes of occurrence of boron in steel which confirm the view taken by Monsieur Kohn.

Over the last eight years, during which several hundred experimental boron steels have been made, it has been found that boron can occur in two forms, *i.e.* acid-soluble and acid-insoluble. It was found also that the relative amounts of those two forms may vary according to steelmaking conditions, and in some cases the heat-treatments ; nevertheless, the maximum amount of insoluble boron which we have been able to find—even in steels containing up to 0·08% of boron—is of the order of 0·004%. We are dealing with steels in which the nitrogen content is of the order of 0·005%. The close similarity in the levels of these two elements indicated that the insoluble compound might be boron nitride, and five years ago we obtained some confirmation of this suggestion. Table B shows four steels—two ferro-boron treated with low and high boron level, and the other two Silcaz-treated, again with low and high boron level, from which non-metallic residues have been extracted by the Dickenson method. The main part of the residue from the ferro-boron-treated steels is Al_2O_3, but the most interesting features are the boron and nitrogen values in the dried residue. The calculated ratio of boron to nitrogen agrees very closely with the formula BN. There is, therefore, good evidence for suggesting that the insoluble compound is boron nitride. It is interesting to note that from the other two steels, although there was no boron in the dried residue, there was a certain amount of nitrogen. It was shown later that the main part of the residue from the Silcaz-treated steels consisted of silicates, with titanium and zirconium nitrides and carbides—not boron nitrides.

For high yield stress in 0·5% Mo steel, the presence of soluble boron, of the order of 0·0015%, is necessary. Table C, which gives the selection of steels, is taken from the authors' Table II, and shows how it is possible to vary the ratios of soluble and insoluble boron. In steels *F*, *G*, and *H*, an increase of the ferro-boron additions increases the amount of soluble and insoluble boron ; the latter, however, seems to reach a maximum of 0·0025%. The first four steels were treated with decreased amounts of Silcaz, and, as the amounts of boron, titanium, zirconium, etc., are decreased, the insoluble boron increased

Table C

VARIATIONS OF ALUMINIUM, TITANIUM, AND BORON IN FORTIWELD

Composition : 0·13% C, 0·5% Mn, 0·4% Si, 0·5% Mo

No.	Steelmaking Additions				Boron, %		L.R.C., °C./min.
	Al, %	Ti, %	Boron		Soluble	Insoluble	
			%	Alloy			
A	0·024	...	...	...	nil	nil	>180
B	...	...	0·003	Silcaz	0·0031	0·0002	25
C	0·012	...	0·002	,,	0·0010	0·0008	>180
D	0·024	...	0·001	,,	0·0002	0·0008	>180
E	0·03	...	0·0005	,,	0·0003	0·0002	>180
F	0·024	...	0·003	FeB	0·0007	0·0016	>180
G	0·024	...	0·006	,,	0·004	0·0025	25
H	0·024	...	0·010	,,	0·006	0·0022	40
I	0·05	...	0·003	,,	0·0006	0·0013	>180
J	0·024	0·06	0·003	,,	0·0031	nil	35
K	0·05	0·06	0·003	,,	0·0031	nil	40
L	0·024	0·03	0·003	,,	0·0024	0·0007	30
M	0·024	0·09	0·003	,,	0·003	nil	35
N	0·024	0·06	0·006	,,	0·0061	0·0001	70

and the soluble boron decreased. Where only 0·0005% of boron is added the insoluble boron is, of course, very low.

These results, and many more, have shown that high soluble boron is needed to improve the yield stress, and this can be obtained in several ways. The ferro-boron addition may be increased to give a higher boron content than usual when using Silcaz. Thus, in a steel killed with aluminium, a ferro-boron addition, equal to 0·006%, would give 0·004% of soluble boron, and would show the enhanced mechanical properties. Again, the effect may be obtained by adding the normal boron as ferro-boron if titanium and aluminium are also added.

Those elements which appear to assist the action of boron, such as titanium and aluminium, are themselves strong nitride formers, and our views on the occurrence of boron in steel are based on the relative affinities of these elements for nitrogen. The main outlines of these ideas are illustrated by the three examples in Table D, using a 0·5% Mo steel, with : (*a*) Ferro-boron to give a boron addition of 0·003% ; (*b*) the same ferro-boron addition with aluminium (0·01%) ; and (*c*) 0·003% of boron, with 0·04% of aluminium and 0·06% of titanium in the amounts provided by the normal Silcaz addition. The nitrogen content is assumed to be normal, say, 0·005%. In cooling these steels from the liquid state there will first be such formation and separation of nitrides as would be possible in the liquid state. There will also be precipitation of nitrides in cooling below the solidus, depending upon the amount of the elements present and on their affinity for nitrogen, and on rate of cooling, *i.e.*, the time available at temperature for the precipitation reaction.

The three elements titanium, aluminium, and boron have a decreasing order of affinity for nitrogen, and this order, as suggested in Table D, would in fact be the order of preferential precipitation of nitrides. There may also be a difference in temperature of precipitation, but apart from that, the difference in affinity will result in one element taking nitrogen at the expense of the others.

In the first example, the only nitride possible is boron nitride, the amount of which will depend on the amount of boron and the rate of cooling. With slow cooling there will be maximum formation of boron nitride, which will result in almost complete elimination of the nitrogen present. Under such conditions, there will be only a small amount of residual soluble boron, and that steel would not show the mechanical properties. On reheating such a steel, as for annealing and normalizing, there would be no change in the amount of insoluble boron, and, of course, in that of soluble boron. Increased yield stress from such a steel would only be obtained with an increase in the initial boron addition, which should be of the order of 0·006%. With 0·006% of boron and 0·005% of nitrogen, there should still be, even at a maximum formation of boron nitride, a fairly high residual soluble boron, which would give the properties.

In the second example, the presence of aluminium in the cooling from the liquid state will result in the formation of aluminium nitride preferentially to that of boron nitride. The use of aluminium thus results in a decreased amount of the insoluble boron and an increased amount of soluble boron. If such a steel were cooled faster there would be less time available for the formation of aluminium nitride, and consequently more soluble nitrogen for the reaction with boron, so that at room temperatures, the amount of soluble boron would be slightly higher than after a normal slow cooling. If such a steel were reheated for normalizing, the boron reaction would recommence, and more boron nitride and a lower soluble boron content would result. This steel also would not show the enhanced properties, but it would show the properties if either the boron addition or the aluminium addition were increased within certain limits.

The third example illustrates the presence of titanium, which has a very strong affinity for nitrogen, and which will lead to the formation of nitrides even in the liquid state ; further cooling will give further formation of titanium nitride. In this case, there may be such a removal of nitrogen from the steel that the amount left would yield only a small amount of aluminium nitride and no formation, or only a very minute formation, of boron nitride. Those are the conditions which give the maximum soluble boron, and which are needed to obtain the enhanced mechanical properties. Because of the high nitrogen affinity of titanium, fast cooling would not substantially modify the amount of soluble boron.

To obtain high yield by means of boron additions, it

Table D

OCCURRENCE OF BORON IN STEEL

	B 0·003%		B 0·003%, Al 0·04%		B 0·003%, Al 0·04%, Ti 0·06%	
Condition of steel after solidification	Solid solution		Solid solution		TiN + solid solution	
	Slow	Fast	Slow	Fast	Slow	Fast
Effects on cooling precipitation of :						
TiN	...	...	...	...	High	Lower
AlN	...	...	High	Lower	Low	Higher
BN	High	Lower	Medium	Very slightly lower	Minute	Minute
Boron remaining in solution, %	Low (<0·0005)	Higher (0·0005–0·001)	Medium (0·0006)	Very slightly higher (0·001)	High (0·003)	High (0·003)
Effect on reheating for annealing	No change	Decreased soluble boron	No change	Decreased soluble boron	No change	No change

seems that it is necessary to prevent the formation of boron nitride, as otherwise the effectiveness of the boron is lost. The elements aluminium, titanium, and zirconium may, therefore, be regarded as ' boron protectors ' owing to their greater affinity for nitrogen. Naturally, with steels of high nitrogen content, greater amounts of these boron protectors are needed, and that, I suggest, is the reason why Dr. Dickie did not obtain the properties he expected. He has admitted to using basic Bessemer scrap. Consequently, his nitrogen content would be high, and to obtain the effect from boron he would need to have present more boron than he probably had.

The precise nature of the effect of soluble boron, and the reason it gives this effect, is a subject for speculation. It is known that molybdenum steels are prone to show either a high temperature (850–800° C.) or a low temperature (650–600° C.) of ferrite formation, depending upon whether the cooling is slow or fast. When transformation occurs at the lower temperature, the distribution of ferrite is acicular, with interspersed carbide, *i.e.*, the structure associated with the enhanced mechanical properties. Soluble boron, then, merely acts to delay transformation to the lower temperature. In other words, a certain amount of hardening with a 0·5% molybdenum steel can be accomplished in one of two ways—either by fast cooling, or by the addition of the correct amount of boron under the correct conditions, which permits the hardening to be obtained from more normal rates of cooling. The addition of soluble boron is thus equivalent to a decrease in cooling rates, which produces hardening by nucleation similar to that at fast rates of cooling.

Professor **H. O'Neill** (University College, Swansea) : I am glad that somebody is tackling the problems associated with boron, because it is a sensitive element and a little will go such a long way. When one reads in the paper that 0·0016% of boron doubles the yield stress, one realizes the potentialities of the element.

Some time ago the question arose of whether boron should be introduced into commercial cast iron, but the matter was not pursued. Do the authors believe that the return of boron steel scrap into industry might lead to the upsetting of programmes and of specifications ?

The boron steels which the authors mention are chiefly characterized by high impact values, except in the un-normalized thick plates ; and since the steels have to be deoxidized I should like to ask whether they have inherent fine grain sizes and what are their ageing characteristics. It might be imagined that the high impact values and the deoxidation implied that the casts, in general, had inherent fine-grain sizes, but the French paper previously mentioned (Potaszkin) indicates that boron has the effect of facilitating austenite grain growth, which seems to be a contrary indication. It is not usual to have an inherent fine-grain steel, in the ordinarily accepted sense, which at the same time is liable to exaggerated austenite grain growth unless the growth threshold temperature is very high. I wondered whether the authors knew if the thick plates, in Table III, with 40 tons/sq. in. tensile strength but impact values of only 5 ft.lb., had a very coarse crystal size, both actual and inherent. It would not be desirable to put 5-ft.lb. material into certain kinds of service.

On p. 289 it is reported that the surfaces of the commercially produced steels were " fair to good." Were any fatigue tests carried out on the black plate ? I do not suppose that boron gives a sticky surface scale, but can any amplification be made about the surface of plates rolled from these alloys ?

The theory of the effect of boron has been dealt with in a very interesting way by several speakers. I understand that boron is in the interstices of the austenitic lattice, and I suppose that nitrogen is, too. Whether in the γ condition these two elements interfere with each other or play a special rôle I do not know. Since the steels made by the authors have very good welding properties, do they have any views on whether boron controls hydrogen, which is also an interstitial element at high temperatures, and which is believed to be responsible for cracking ?

In regard to the nitrogen content of the steels, I wonder whether the process is applicable, or only after some further modifications, to Bessemer steels.

We should be grateful for any high-tensile weldable steels. There was previously a titanium-bearing high-tensile steel from the same stable. Titanium also has a special relationship with nitrogen, but not so much is heard about this titanium steel now. Does the addition of boron give rise to any practical difficulties in steel-making ?

CORRESPONDENCE

Mr. **J. Dearden** (British Railways) wrote : I have had the opportunity of testing a sample of ½-in. plate, the analysis of which corresponds with that given on p. 288 of the paper. The yield stress and maximum stress were about 90% of the values given for ½-in. plate in Table IV, the elongation and reduction in area were appreciably higher, and the izod impact value 40% higher. Four Reeve fillet-weld cracking tests had been made, using mild-steel electrodes, and the hardness and absence of cracks in the heat-affected zone confirmed the author's results. Small root cracks in the weld metal were observed in 10 out of 12 sections.

It is interesting to compare the weldability of the new steel with that of the conventional low-alloy structural steels. For the same degree of hardening in the Reeve test, the new steel is equivalent to steels containing 0·23% of carbon and 1·4% of manganese, or 0·6% of molybdenum. Both of these steels cracked in the Reeve test when welded with the small fillets which failed to crack the boron–molybdenum steel, and their tensile properties are inferior. To obtain the same tensile properties it would be necessary to raise the carbon to about 0·3% in the conventional low-alloy steels, but this would render them unweldable without pre-heating.

The powerful influence of boron on the hardenability of low-carbon molybdenum steel is seen in the high values of hardness attained in the Reeve test. From personal experience of this test I estimate that 0·14% of carbon would be required to take the place of the 0·003% of boron for equal hardness in the Reeve test. This suggests that boron is about 45 times more potent than carbon in these circumstances.

Since, as the authors have shown, even 0·0016% of boron is sufficient to double the yield point, I think some consideration should be given to the effect of scrap on furnace charges before the steel is produced in large quantities.

Have the authors observed and identified a golden-coloured inclusion, usually of cubic form, which occurs at isolated spots in the microstructure of this steel ?

Dr. **J. R. Rait** (Messrs. Hadfields, Ltd.) wrote : A short time ago we learnt from the authors something of the interesting properties of this 0·5% molybdenum–boron steel, and we have carried out some preliminary tests on the material in the cast form. The object was, of course, to see how far the results obtained on the wrought material were realizable in the cast form.

Two experimental casts of low-carbon 0·5% molybdenum steel were melted in a 2-cwt. high-frequency induction furnace. These casts were similar in all respects, except that, to one of them, a boron addition of 0·003% was made, the boron being introduced in the

Table E

TENSILE AND IMPACT TESTS ON LOW-CARBON 0·5% MO STEEL WITH AND WITHOUT BORON ADDITIONS

B, %	Condition	Proportional Limit, tons/sq. in.	Proof Stress, tons/sq. in.			Maximum Stress, tons/sq. in.	Elongation on 2 in., %	Reduction in Area, %	Yield Ratio	Izod, ft.lb.	Brinell No.
			0·1%	0·2%	0·5%						
0·003	As-cast	20·5	29·4	33·0	37·2	45·2	8·5	13·5	0·82	6, 7, 7	215
0·001	As-cast	9·5	16·9	19·0	21·3	32·2	11·0	15·2	0·66	4, 4, 6	143
0·003	950° Air	17·2	27·2	29·6	32·9	42·0	11·0	22·0	0·78	49, 46, 44	207
0·001	950° Air	10·5	16·2	16·3	16·5	30·2	25·2	44·3	0·55	15, 14, 12	133

form of Silcaz, after deoxidation with aluminium, in the manner recommended by the authors. Casting temperatures and conditions generally were practically identical for the two melts, which were cast in the form of standard clover-leaf test bars.

The compositions of the respective casts were :

	C, %	Si, %	Mn, %	Cr, %	Ni, %	Mo, %	B, %
Boron treated	0·14	0·33	0·61	0·09	0·07	0·57	0·003
Without boron	0·14	0·14	0·61	0·06	0·07	0·57	0·001

Tensile and impact tests were made both in the as-cast and normalized conditions. The results are given in Table E. These results clearly demonstrate the influence of the boron addition in enhancing the yield stress and tensile strength, and are in good agreement with the effect reported by the authors on forged material. The impact value also shows some improvement, slight in the as-cast condition, but very definite after normalizing.

It should be emphasized that these are the results of preliminary tests only, and it should not be assumed that they are necessarily representative of the properties of this class of steel in the cast form. They are, however, considered sufficiently interesting to warrant further investigations, which are proceeding.

AUTHORS' REPLY

Mr. **W. E. Bardgett** and Dr. **L. Reeve** wrote in reply : As Dr. Allen has stated, the effect of boron is to suppress the separation of the coarse ferrite, but it should be emphasized that the critical nature of molybdenum, and the realization of the effect of boron on materials which have a low carbon content and are not hardened and tempered, have not previously been demonstrated. Our paper is strictly practical and does not go into the fundamentals of the subject, although these are receiving attention. The conditions for obtaining the desirable properties in the molybdenum–boron steel are not critical, as Dr. Allen has suggested, though they may be when additional elements are present.

Dr. Dickie's remarks have been almost completely answered by the contributions of Monsieur Kohn and Mr. Speight. His failures obviously were caused by the boron being rendered ineffective by combination with nitrogen in the Bessemer steel scrap. There may be some points which will require investigation, but it appears that, knowing the composition of the base material, and with the knowledge gained from our further work, we could be fairly certain of the procedure necessary to achieve the desired properties.

The copper content of the molybdenum–boron steels made at the Appleby shops is very low. The most recent figure was 0·027% of Cu, which is approximately the content of the steel tested by Dr. Dickie.

It is interesting that Monsieur Kohn has substantiated our work so far as soluble boron is concerned. We also note that, when using a high-nitrogen steel, he has had to increase the ferro-boron addition, and that when a certain ferro-boron addition is reached, adequate properties can be expected.

Mr. Speight's facts and ideas about the rôle played by the titanium, the aluminium, and the boron are enlightening, and this work will no doubt be extended.

The effects of the return of boron steel scrap into industry, mentioned by Professor O'Neill, are not a matter for concern, because the boron will be oxidized out of the steel.

The austenitic grain size of the 1-in. plate mentioned was 7–8. Incidentally, the austenitic grain size in a 15-in. square bloom of Fortiweld steel, cast 23770, was 5–6. As far as actual grain size is concerned, this may be judged from Fig. 19 of the paper.

The term " fair to good," which was used to describe the surfaces of the commercially produced steels, was taken from a mill report, and its correct interpretation, so far as alloy steel plates are concerned, is that the surfaces were perfectly satisfactory for an alloy steel. We have not carried out fatigue tests on actual plates with the original surface present, but tests on specimens machined from plates have given remarkable results, with fatigue ratios of the order of 0·63, compared with a normal figure of about 0·5. We do not know why this should be ; it is not altogether characteristic of this steel alone but appears in certain other steels of a similar type.

Professor O'Neill's point about the possible influence of boron on hydrogen in the steel is of considerable theoretical interest and may account for its lack of sensitivity to cracking after welding, but it has not yet been investigated. The boron steel does not suffer from the same practical steelmaking troubles which arise in the exploitation of the titanium-bearing steels developed in this country in 1937.

We are grateful to Mr. Dearden for his confirmation of the good welding properties of these steels and, in particular, their resistance to cracking in the weld-hardened zone. The small root cracks in the weld are caused by the type of electrode used, but it is possible to obtain commercial electrodes which are free from this tendency.

The golden-coloured inclusion seen in the microstructure of the steel is most probably either titanium cyano-nitride or titanium nitride.

We thank Dr. Rait for his results, which not only confirm our data on the tensile strength and yield stress of the wrought material, but also show that boron has the effect of increasing the impact value of normalized castings.

Joint Discussion on the Papers—

FURTHER X-RAY STUDY OF THE EQUILIBRIUM DIAGRAM OF THE Fe–Ni SYSTEM*

by E. A. Owen and Y. H. Liu

FREE-ENERGY AND METASTABLE STATES IN THE Fe–Ni AND Fe–Mn SYSTEMS†

by F. W. Jones and W. I. Pumphrey

MICROSCOPICAL STUDIES ON THE IRON–NICKEL–ALUMINIUM SYSTEM PART I—α + β ALLOYS AND ISOTHERMAL SECTIONS OF THE PHASE EQUILIBRIUM DIAGRAM‡

by A. J. Bradley

and CONSTITUTION OF IRON–NICKEL–CHROMIUM ALLOYS AT 650° TO 800° C.§

by W. P. Rees, B. D. Burns and A. J. Cook

Dr. **A. H. Sully** (Fulmer Research Institute), Dr. **F. W. Jones** (Brown-Firth Research Laboratories), Dr. **W. W. Marshall** (B.S.A. Group Research Centre), and Mr. **W. P. Rees** (National Physical Laboratory), introduced the papers.

Dr. **G. V. Raynor** (Birmingham University): Dr. Bradley's paper records a very fine piece of metallographic research. Micrographic effects have been observed, and have been interpreted on the lines of the previous X-ray knowledge, so that Dr. Bradley has been able to deduce from a given micrograph rather more than the micrograph alone could have told him. A number of alloys have been examined, and in Dr. Bradley's hands the whole research has been made to conform to a consistent picture, and to give a result which appears to be substantially correct. The procedure, however, is semi-intuitive, and is, perhaps, hardly to be recommended because, in inexperienced hands, the danger of misinterpretation is not negligible.

The author, on p. 26, says that the phase rule must be regarded as of more importance than the actual appearance of individual micrographs, which do not always observe the rules. Surely the reverse is true.

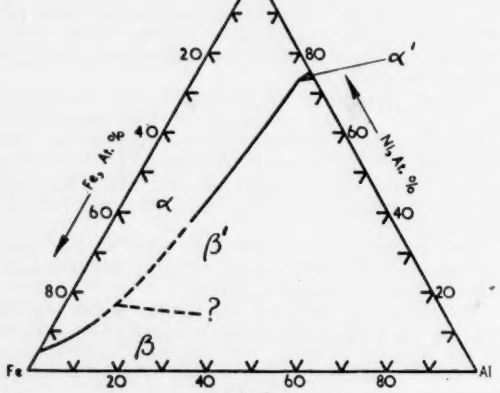


Fig. A—Ternary diagram of the iron-nickel-aluminium system

The phase rule is a very useful guide to what may be expected, and, if alloys do not fit in with its requirements, there is every reason to suspect that something is wrong and to reinvestigate with greater care, those particular alloys or composition regions; but to assume that the alloy is wrong, and that the phase rule is right, is somewhat dangerous, because it may obscure some important new phenomenon. It may be remembered that the nature of the order–disorder change in certain alloy systems was, to some extent, obscured at the outset by attempts to make the facts fit the phase rule. I would say that what really matters in constitutional work is the experimental data; if they do not fit the rules, then they should be rigorously re-examined, but not coerced.

The requirements of the phase rule have played a large part in the construction of the isothermals on p. 27. It is upon phase-rule requirements that the $(\beta + \beta')$ field above 1050° C. really rests, because at 1150° C. there is a β alloy right in the middle of the $(\beta + \beta')$ field, and at this temperature there is only one three-phase $(\alpha + \beta + \beta')$ alloy. Incidentally, it is a pity that no $(\beta + \beta')$ or $(\alpha + \beta + \beta')$ alloys are illustrated in the micrographs. Above 1050° C., therefore, it appears that the $(\beta + \beta')$ field is included mainly to make a sensible proposition of a peritectic reaction liq. $+ \beta \rightleftharpoons \alpha + \beta'$ at 1350° C.

By making a sketch map of the projected surfaces of primary separation (Fig. A), what happens near the FeNi and NiAl sides of the ternary triangle may easily be interpreted, but what happens in the body of the triangle is more problematical. If, as is stated, there is a reaction involving liquid, α, $\beta + \beta'$, then there must be a line in the projection dividing the primary β and primary β' fields. There does not seem to be much evidence of that in Fig. 32 of the paper. What, therefore, is the true relationship at the liquidus temperatures between β and β'? If β and β' are so much alike that they form one phase field over most of the isothermals, with no discontinuous change in lattice spacing, a sharp division between the fields where β and β' separate from the liquid as primary particles would hardly be expected. I feel that this is a case where the experimental results should take priority and not be coerced to fit the phase

* *Journal of The Iron and Steel Institute*, 1949, vol. 163, pp. 132–137.
† *Ibid.*, 1949, vol. 163, pp. 121–131.
‡ *Ibid.*, 1949, vol. 163, pp. 19–30.
§ *Ibid.*, 1949, vol. 162, pp. 325–336.

rule, and where the continuance of the ($\beta + \beta'$) gap right up to the solidus temperatures should be considered as not really proved.

This raises another point, namely, to what extent are ordered and disordered structures with the same basic crystal structure to be considered as the same phase or as different phases? In the diagrams shown, at more than 30 atomic per cent. of Al, it appears that a path can be traced from the Fe–Al axis to the Ni–Al axis without any discontinuous change in the lattice spacing or type of ordering. Similarly, on passing along the 10% Ni line in the β field there is no discontinuous change, but on skirting the aluminium-rich boundary of the two-phase regions there is a discontinuous change, and I think that this necessitates a true two-phase gap, in accordance with the phase rule. This gap, however, shrinks very markedly as the temperature rises. There is a big difference between the extent of the ($\beta + \beta'$) field at 950° C. and at 1050° C. At 1050° C. the gap is extremely small, and there must be only a very small difference indeed between the lattice spacings and ordering of the two phases, β and β'. It is difficult to believe that this small difference is perpetuated at still higher temperatures, considering the changes wrought by increasing the temperature from 950° to 1050°. It would appear rather more probable that this small difference would disappear, and that at high temperatures the β (β') field is really continuous.

All this work has been carried out with quenched alloys, and the author points out that the use of quenched filings in X-ray work may be misleading. The use of quenched micro-specimens may also be misleading, owing to the occurrence of transformations on quenching. It would have been a good plan for the author to have checked the results with a high-temperature X-ray camera, and I hope that this may be done. Cameras which are able to work at the very high temperatures involved do exist in this country.

In relation to the type of diagram shown on p. 27 of the paper, an interesting point is that the initial path, starting at the iron-rich end of the aluminium-rich boundaries of the two-phase fields, is directed to almost exactly 50% of Ni and 50% of Al; this tendency is even more striking at the lower temperatures. Has Dr. Bradley any idea why this is so?

The paper on the Fe–Ni–Cr system is a more conventional piece of work, in which it is pleasing to see that X-ray and micrographic work are both used, and agree not too badly. Proceeding in this way, it is possible to see the limitations of the methods; for instance, the microstructure of 5F22 is quoted as showing, after 156 days at 650° C., the phases α, γ, and σ, whereas the X-ray pattern shows only supersaturated α. Another lesson may be learned from the constitution of filings made from duplex alloys. Figure 41 shows how the proportion of the two phases can vary in the separate particles if the grain-size is fairly large. The authors' practice of using filings from a homogeneous alloy and heat-treating these is to be recommended as a general practice wherever it is possible.

It has been known for a long time that cold-work before annealing hastens the attainment of equilibrium, but the factor 6×10^3 quoted on p. 333 seems abnormally large. Have the authors anything to say about that? In the meantime, it is important to note the effect.

Another good feature of the work is that an examination has been made of the mechanism by which equilibrium is approached. This is a feature which would repay further study in several other systems, because it is linked with the relative free energies of the various possible phases which can occur, and might give information about these quantities in a rough and ready way which cannot be obtained by other methods. From the diagrams on p. 334, it appears that the σ phase can take up more Ni than the 5% which was suggested earlier by Bradley and Goldschmidt's diagram. Further, the Ni content increases with temperature, and it is a pity that the experiments stopped at 850° C., because I should like to know what happens at higher temperatures right up to the limit of stability of the σ phase in the binary diagram, since it is known that in the Cr–Co–Fe system at 800–850° C., there is a continuous solid solution field between the two σ phases, and that in the Cr–Co–Ni system at 1200° C. the σ phase of the Cr–Co diagram extends so deeply into the ternary diagram that well over half the Co in it may be replaced by Ni, with little change in the Cr content. There seems to be a tendency towards the formation of a σ phase in the Cr–Ni system, which is not realizable until the appropriate amount of Co is present.

Professor Owen and Dr. Liu have made further investigations into the Fe–Ni diagram to settle discrepancies between earlier work at Bangor[1] and investigations by other methods. The paper calls for little comment, but I must commend the attention given to details of technique and the use of a high-temperature X-ray camera to work out the ($\alpha + \gamma$)/γ-phase boundary, thus avoiding trouble caused by partial or complete transformation to α_2 on quenching. The authors have calibrated the sensitivity of their method in detecting small amounts of α and γ in the appropriate alloys. This is another point which might be taken up in other work, and similar checks might be made on other systems where this method is used. It is also comforting to note that the results from filings and from lump specimens give the same answer in this case.

The authors suggest that the difference between their results and those obtained by the magnetic method may be caused by the existence of long-lived metastable states. This phenomenon is possible, and may occur more often than is recognized. In a system which approaches equilibrium sluggishly there may be other states with free energies not very much above those of the equilibrium state, and as the alloy relaxes towards equilibrium it may very well take up a spurious temporary 'equilibrium' between one of the equilibrium phases and something which does not belong to the diagram at all. If the latter is long-lived, it may be mistaken for an equilibrium constituent. The results would be interesting if the authors could undertake an investigation of this postulated metastable state, possibly by high-temperature X-ray photographs after successive intervals of annealing at appropriate temperatures in this composition range.

The thermodynamical investigation by Dr. Jones and Dr. Pumphrey uses the results of Owen and Liu to calculate thermodynamical quantities to be used in investigating the diffusionless transformation $\alpha \rightleftharpoons \gamma$. Lest anyone should be misled by the excellent agreement between theory and experiment in Fig. 2, it should be emphasized that this is inevitable in the absence of arithmetical errors.

The application of the thermodynamics in the appendix leads to the deduction of two different values from two different equilibrium diagrams for the value of ΔFe, the free-energy difference between α and γ iron. Because of this, one must agree with the authors that the assumptions involved in this type of free-energy calculation need re-examination before a great deal is based on them, and it would be interesting to hear whether they have considered making it more rigorous. Even though the conclusions are somewhat qualitative, there is no escape from the main conclusion that there is some sort

of energy barrier to be surmounted to make the transformation work at all. The authors themselves suggest that this is connected with the shear mechanism of the lattice changes, face-centred cubic to body-centred cubic and back again, and that it has nothing to do with elastic strains caused during transformation. I think that this is quite probable ; we know of another shear mechanism which turns a body-centred cubic lattice into a face-centred cubic structure, and it occurs when body-centred lithium transforms to face-centred cubic lithium at the appropriate sub-zero temperature. It is facilitated by deforming the specimen during the transition. Have the authors considered transforming their specimens while they are being deformed, because, if the energy barrier is essentially connected with the shear process, the transformation ought to be facilitated by the deformation ?

Dr. **N. P. Allen** (National Physical Laboratory) : I have two interests in the paper by Dr. Jones and Dr. Pumphrey. The first is to see whether, by thermodynamical calculations, we can avoid the tedious experimental determination of equilibrium diagrams, and the second is to find out something more about what governs the rate of transformation in alloys.

A great deal of work has been done on the effect of carbon on the rate of transformation of steel, and it has been theoretically treated on the basis that the diffusion of carbon is the controlling factor ; but when the effects of alloying elements on the transformation in relation to their effect on the diffusion process have been studied, little progress has been made. Consequently, in this investigation, it was decided to study the influence of alloying elements on the transformation in the absence of carbon, to see how far we could go.

Further, since the free-energy changes play a large part in modern theories, we considered that it would be desirable to obtain an idea of the actual magnitudes of the free-energy changes involved. A number of assumptions had to be made, but it has been found possible to obtain from the equilibrium diagram and thermal data an approximation to the desired values. Certain risks were involved, but, as will probably be mentioned later in the discussion, further work based on experiment suggests that the calculations have not been too misleading.

The transformations in both series of alloys on continuous heating and cooling have the characteristics of almost instantaneous and diffusionless shear transformations. They do not occur as soon as the free energy of the alternative phase becomes less than that of the existing phase, but are delayed until some resistance to transformation is overcome. The interest of the work lies in the evidence which it affords of the nature of this resistance. It cannot be a simple mechanical resistance to a shear, for the resistance is apparently as great for a transformation occurring on heating at 600° C., when the alloy is comparatively soft, as for the cooling transformation at 200° C., when the alloy is hard. It must be strongly influenced by the composition of the alloy, being practically zero for pure iron, and quite high for a 30% Ni alloy. The problem is to find a source of resistance to transformation which possesses these two characteristics.

In making the free-energy calculations it was necessary to decide between alternative equilibrium diagrams for the Fe–Ni system, and the authors were fortunate in having access to the work of Prof. Owen and Dr. Liu, which is now published in the first of the four papers under discussion. Professor Owen's work has been most valuable, and where it has been checked it has been found to be correct. A confirmation of the position of the α boundary is recorded in the paper by Dr. Jones and Dr. Pumphrey, and confirmation of the position of the γ boundary has recently been obtained by microscopic methods.* Hitherto such methods have not been very successful in this system, but by prolonged annealing of pure alloys in the temperature range 750–500° C. it is possible to get structures in which the α and γ phases can be clearly distinguished, and consequently an idea of the course of the $\alpha + \gamma/\gamma$ boundary can be obtained. At 643° C. Prof. Owen and Dr. Liu place the γ boundary at 13·5% of Ni, but we place it slightly higher, between 13·7 and 14·6% of Ni. In general, our results are a little higher than theirs, but, because of the way in which our work has been done, we should emphasize the closeness of the agreement rather than the slight differences.

In regard to the diagram by Messrs. Rees, Burns, and Cook for the Fe–Ni–Cr system, I myself have been very interested in the comparison of the two experimental methods, and my conclusion is that there is very great danger, in work of this kind, in relying on one method alone. The precipitation of α from a single-phase γ alloy, and its gradual conversion to σ, as shown in Figs. 42 to 45 of the paper, is one of the striking results of such a comparison.

I have also been impressed by the great variety of the structures observed. In the massive forms, illustrated in Figs. 13 and 15, σ is clearly undesirable, but it is by no means so certain that σ is equally objectionable in the finer forms illustrated, *e.g.*, in Figs. 35 and 36, or in the moderately massive, but evenly distributed, form shown in Fig. 45. It is important, for the logical development of steels for use at high temperature, to obtain clear information on such points, and to make the necessary systematic tests.

I was interested to notice that Dr. Bradley, who has been so great an exponent of the X-ray method, had, in his present paper, relied almost entirely on the microscope. Because of the great directness of the X-ray method it should be considered decisive in the last resort—where doubt exists. If someone claims to have found a new phase in a diagram, it is incumbent upon him to show that it has a lattice which is different from the lattices of the other phases. Nevertheless, although the final decision lies with the X-ray method, the microscope has many advantages in the sensitivity and the breadth of information that it gives, and is most valuable in the hands of the experienced worker.

Dr. **K. Hoselitz** (Permanent Magnet Association) : Professor Owen and Dr. Liu's arguments, supporting the view that a close approximation to the true equilibrium diagram is arrived at, are inconclusive. For instance, in the determination of the γ boundary in plate specimens, alloys of 33·97 and 37·24 atomic per cent. of nickel were used, being subjected to alternative annealing at 400° C. and cold-working at room temperature. In my opinion, this alternating treatment is not necessarily effective in accelerating the attainment of equilibrium at 400° C. From equilibrium phase diagrams suggested in the present paper or in other work,[2] it can be inferred that at room temperature both these alloys are in the two-phase field. In fact, it is clearly shown by magnetic work[3] that an initially single γ-phase 35% nickel alloy shows both α and γ after cold-work at room temperature. Heat-treatment at 400° C. for from 2 to 11 days, between successive stages of cold-work, would not be sufficient to produce equilibrium after such phase separation by cold-work at room temperature, and, therefore, the result of the experiment in the present paper cannot be regarded as giving information about the true equilibrium state in lump specimens at 400° C.

* Unpublished Work.

Similarly, alloys with 8·56, 9·55, and 12·16 atomic per cent. of nickel, cold-worked at room temperature, may be made heterogeneous by this treatment of cold-working. Fluctuations in composition—a possibility mentioned by the authors when they refer to a possibly uneven distribution of the γ phase in the plates—may produce certain regions in which a cold-worked plate acquires a sufficient nickel content to become γ during the final heat-treatment of 99 days at 400° C. Cold-work, particularly in Fe–Ni alloys, produces fluctuations in the distribution of atomic concentrations of the constituents. Naturally, in powders the same considerations apply, owing to the heavy cold-work during their preparation—apart from any surface effects.

From the complicated changes occurring in Fe–Ni alloys during cold-work,[3] and the known sluggishness of any changes at low temperatures, it appears that a combination of cold-work at one temperature and heat-treatment at another temperature might cause complex conditions which would not necessarily be of any help in equilibrium determinations.

Both Dr. Sully, in his discussion of my paper,[3] and Prof. Owen and Dr. Liu in their paper, refer to the possible existence of a metastable state during the attainment of equilibrium. If such a metastable state exists, it is difficult to decide whether the long treatments of the authors or the extrapolation to infinite times by Sucksmith and myself[2] approach the true final equilibrium or the metastable state, and it still appears that the difference in the final state, whether metastable or true equilibrium, depends on whether the initial alloys are in the α or γ state.

It cannot be said that extrapolation is more risky than long heat-treatments, especially when it is considered that, in our magnetic work,[2, 4] the heat-treatments at temperatures below 500° C. were of the same order of duration as those quoted by the authors. (The authors' powders were heated for up to 616 days at 350° C., and the solid specimens were heated for 126 days in the α state and for 36 days in the γ state. All our specimens were heated for 150 days at 365° C.). Further, in the present paper, alloys with more than 27% of nickel were left in the γ condition. However, the authors made use of the estimation given by us[2] of the time to approach equilibrium half way from the single-phase α state, although they speak of reaching complete equilibrium without qualification of the initial state.

The authors criticize the magnetic method because of a difference in results reported at an earlier[4] and a later[2] stage of the investigation of Fe–Ni alloys made by Professor Sucksmith and his collaborators. On these grounds almost all methods would have to be rejected, including the one used by the present authors.

In support of the work by Sucksmith and myself, the equilibrium phase boundaries are arrived at by corroborative evidence from a set of alloys of from 0 to 50% of Ni, and quantitative phase analysis of each alloy within this range consistently gave the same phase boundaries. The authors, however, rely on the structure spectra of boundary alloys and the appearance of traces of a second phase in alloys which are reputed to give bad X-ray line resolution. It may reasonably be supposed that fluctuations in composition may occur, which, in a system of the sluggishness of the Fe–Ni system, not only would take extremely long times to cancel, but might even be accentuated by uphill diffusion occurring in local regions of different concentration, especially as the system is one in which the differences in free energy of the two phases at the temperatures in question are extremely small.

The conclusions of the present authors would seem to require support of quantitative phase analysis before they can be accepted as giving true equilibrium states.

Dr. **K. W. Andrews** (The United Steel Companies, Ltd.) : The work of Mr. Rees, Mr. Burns, and Mr. Cook on the Fe–Ni–Cr system provides a basis for the study of many commercial alloys, and especially those in which the possible occurrence of the σ phase has to be considered. The detection of small amounts of σ is one of the main problems which we encounter, and it is one in which we have found the greatest success when we have tried systematically to use microscopic and X-ray methods together.

In our own laboratory we use the microsection itself for the X-ray examination. It is sometimes the practice to do this by using the glancing-angle method, but small amounts of σ may escape detection. An American worker, Barnett,[5] has pointed out that by electrolytically etching the surface of the specimen with ferric chloride it is possible to throw up the σ phase in relief, and thus detect it more readily. This method was tried, but it was thought better to carry on the electrolysis and collect a small amount of residue from the surface and examine it for σ, using the same sample which had been examined under the microscope. In more than one commercial alloy what had been thought to be σ was discovered to be σ plus carbide. This is not an unusual experience. If ferrite is present it usually separates out as well, and that is often very useful.

This technique has become routine, and a considerable number of samples from certain commercial alloys are being examined microscopically. They are then submitted to electrolysis, and the residue is examined by X-rays. The two sets of results in conjunction are much more satisfactory than either alone. If desired, the specimen can be re-examined under the microscope. This combined method might be useful also in fundamental equilibrium studies.

I should like to refer briefly to the α_2 phase. Some samples were examined in which, from the results of the microscopic examination, the α had largely transformed to σ, and yet X-ray examination of the solid specimen showed considerably more body-centred cubic phase (α phase) than was expected. It was wondered whether something in the preparation of the microsection had led to the diffusionless transformation of γ to α, and I would ask whether the authors have had any experience of that. That cold-working does itself bring about this change, even at room temperature, is well known and has already been referred to.

Can Dr. Jones and Dr. Pumphrey say if their method of approach, in conjunction with suitable experimental work, could be applied to the study of the effect of cold-work on the $\gamma \rightarrow \alpha$ transformation ? If the heat produced by cold-work could be measured in a series of alloys, including some which lie in the γ region and some in the $\gamma + \alpha$ region at room temperature, it might be possible to account for differences on the basis of the different free energies of the γ and α phases. Thus, the amount of the energy of cold-work which re-appears as heat, when some of the γ has transformed to α, should be different from that which appears when there has been no transformation.

Dr. **A. H. Sully** (Fulmer Research Institute) : I should like to speculate on the reason for the disagreement between the results of Hoselitz[3] and those of Owen and myself,[6, 7] particularly in relation to the position of the boundary between the γ- and $(\alpha + \gamma)$-phase regions where, at temperatures below 500° C., the disagreement is very marked. The later work of Professor Owen and Dr. Liu and the check determinations reported by Dr. Jones and Dr. Pumphrey show that the Owen and Sully diagram was reasonably correct. Why, then, did Hoselitz's measurements indicate the equilibrium com-

position of the γ phase between 450° C. and 350° C. as being between 30% and 35% of Ni, while the correct value at the lower temperature is 50% of nickel? I think that Dr. Jones and Dr. Pumphrey have indicated the correct reason for this apparently low value when they point out that Hoselitz determined only the composition of the separating phase, while they determined the presence of one phase in a matrix of the other. In discussing Hoselitz's paper, I suggested that there might be a metastable phase of composition about 33% of Ni, and I adduced some evidence from lattice parameter-composition plots which might be considered to support this view. It is interesting to discuss more fully the reason for the existence of a metastable phase at this composition, which corresponds approximately to Fe_3Ni and seems unlikely to result from an order–disorder transformation, as these ratios of iron and nickel are not such as to lead to an easy arrangement by ordering in the face-centred lattice. It has, however, already been suggested by Nix, Beyer, and Dunning[8] that an ordered phase exists at the composition $FeNi_3$ in which, it may be presumed, iron atoms are at cube corners and nickel atoms at face centres. A tendency to an ordered structure at Fe_3Ni, at 25% of Ni, is equally possible. If there were such a tendency to order in the γ phase at temperatures below about 500° C., the free-energy composition curve for the γ phase would be modified from the form given by Dr. Jones and Dr. Pumphrey to a shape more like that given in Fig. B, showing a subsidiary minimum at 25% of Ni, owing to the existence of short-range order in a γ phase of this and adjacent compositions. Between this subsidiary minimum and the true minimum of the free-energy composition curve there must be a region of curvature of the free-energy curve concave to the composition axis, where, between the points of inflection A and B, the sign of d^2f/dx^2 is negative.

The importance of the sign of the coefficient d^2f/dx^2, in relation to nucleation and diffusion, is considerable. It has been discussed by Dehlinger,[9] Borelius,[10] and others, and its importance in relation to the precipitation theory has been described by my colleague Dr. H. K. Hardy.[27] Briefly, it may be shown that in a region of negative d^2f/dx^2, diffusion alone is the rate-determining factor in the early stages of precipitation, and in a region of positive d^2f/dx^2 there is also an activation energy for the correct compositional fluctuation, which represents an energy barrier to be overcome before diffusion proceeds. The point of change from a region of negative to a region of positive d^2f/dx^2 may therefore reasonably be expected o represent a composition at which the precipitation rocess shows some discontinuity involving a slowing up of the approach to equilibrium concentration.

If this concept is correct, an alloy initially in single-phase γ condition at compositions between A and B will, if subjected to a temperature at which the free-energy curves of Fig. B are appropriate, alter in composition comparatively rapidly to the composition corresponding to point B, and then comparatively slowly to the equilibrium composition C. I would suggest that the results of Hoselitz can be explained on the basis that the point of inflection B corresponds, at 450–350° C., to compositions of 30–33% of Ni.

Thus, in the initial stages of precipitation, which would correspond to the rather short heat-treatments (measured by the time scale which needs to be applied to this system) which Hoselitz used, the composition of the γ phase at temperatures below 500° C., in alloys with nickel contents less that that corresponding to point B, would tend to alter relatively rapidly to a composition appropriate to B, and then only very slowly to the composition of C. If the time is insufficient to allow this further diffusion to occur, a determination

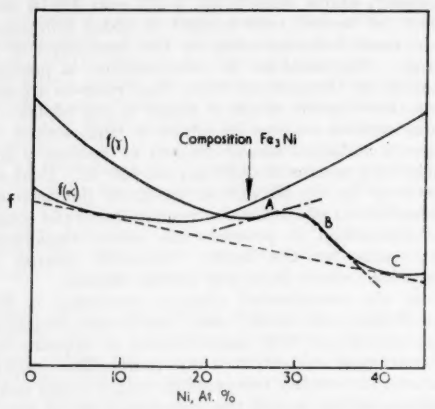


Fig. B—Free-energy composition curves of Fe_3Ni

of the separating phase would indicate a composition close to B. This seems to have been found by Hoselitz, and the lattice parameter-composition plots, which I cited in my earlier comments on Hoselitz's paper, also show abnormalities in this region which support this view.

Between B and C the alteration in composition of the γ phase is very slow. Owen and I[7] studied the fine structure of the lines of the X-ray spectrum of the γ phase for some alloys in this region after heat-treatments at 350° C. We found no change in the sharpness of the γ lines after 89 days of soaking at this temperature. After 186 days, however, the γ spectrum became extremely diffuse, indicating that diffusion to permit the phase to adjust its composition to its equilibrium value had become appreciable only after this lapse of time.

Dr. **O. Kubaschewski** (National Physical Laboratory): I am very interested in the calculations and applications of free energies by Dr. Jones and Dr. Pumphrey. There are interrelations between the free-energy and the equilibrium diagrams of alloys, and these connections can be calculated by making some simplifying assumptions. It must be emphasized quite generally, however, that we have not at present sufficient experimental evidence of the accuracy of such simplifications. This accuracy will, of course, vary from system to system. I should like to draw attention to the objections raised by Darken[11] in the discussion of Zener's paper, of which the present authors are aware. Darken's remarks may be summarized as a warning against over-simplifications in calculations of free-energy relations from equilibrium diagrams.

Consideration of the Fe–Ni and Fe–Mn systems is made easier, since they can be expected to be regular.[12] A number of simplifications made in the present paper are, therefore, valid (though it must be mentioned that this is not necessarily implied by the constancy of ΔH, on p. 130).

Dr. Allen made the same suggestion to us as he did to Dr. Jones and Dr. Pumphrey, namely, that we should investigate the equilibrium diagram of the Fe–Ni system by considering the free energy. The present authors first calculated relative free energies from the equilibrium diagram and then the equilibrium diagram from the relative free energies, but we have sought to determine free energies independently and then to calculate the phase relationships. The method and results have just been published.[13] I should like to mention a few points to show how our work has largely confirmed the assumptions of the present authors.

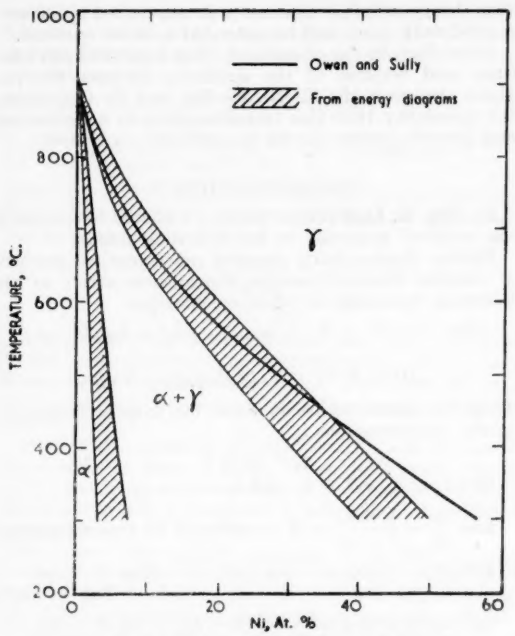


Fig. C—Iron–nickel equilibrium dirgram

The partial molar free energy of solution of iron in Fe–Ni alloys was determined by measuring the H_2O/H_2 ratios in contact with various Fe–Ni alloys, whereby ferrous oxide was formed. The method was similar to that used by Grube and Flad[14] for the thermochemical investigation of Cr–Ni alloys. Our measurements enabled us to evaluate the energy data of γ Fe–Ni. It was found that the entropy of solution agrees within the limits of experimental accuracy with the formula for regular solutions, as was assumed by the present authors (equation (10) in their paper). The heats of formation in the α phase were obtained from those of the γ phase and from reliable heat-content measurements carried out by various observers. The approximate validity of Neumann-Kopp's rule (assumed by the present authors) was, in our case, derived from Zuithoff's work,[15] only a small correction being necessary. A formula was evaluated from the literature for the free energy of transformation of γ to α iron below 1000° C. Whereas the present authors state that this free energy is higher than that given by Zener by a constant amount (25%), we also found higher values which deviated from Zener by amounts which varied with temperature. The only assumption which was retained in our calculations was that of an ideal entropy of mixing in the α phase, which could not be determined experimentally, but should introduce practically no error, as this behaviour was established for the γ phase.

From the results, the free-energy curves of α and γ Fe–Ni were computed, and the phase boundaries (obtained in a way similar to that described by the present authors) are shown in Fig. C, compared with Professor Owen and Dr. Liu's experimental curve. The shaded area does not represent the absolute, but the relative error of thermochemical measurement, excluding all errors which are compensated for by calculation.

This curve was obtained entirely without the use of phase-boundary data, and the agreement must, therefore, be considered to be good. I should like to emphasize, however, that the application of our thermochemical results has been very much simplified, since the solid Fe–Ni alloys form regular solutions. Otherwise, evaluation might have been more difficult, as the thermochemical method applied has its limits in accuracy, and very accurate measurements are required if the method is to be of use. However, systems with pronounced deviations from regular behaviour, *i.e.*, systems in which strong binding forces prevail, will generally also exhibit pronounced thermal effects, and will thus be better investigated by thermal analysis. On the other hand, systems with small energy differences (and slow attainment of equilibrium) will be approximately regular more often, and can be investigated more simply by energy considerations; but such investigation requires a good deal of practical experimental experience, and any result obtained by pure calculation, involving too many assumptions, should be regarded as no more than a first approximation.

Dr. **A. Taylor** (The Mond Nickel Co., Ltd.): Throughout his investigation Dr. Bradley has used iron, nickel, and aluminium of high purity, and, by employing substantial annealing periods, has probably succeeded in approaching very closely to true equilibrium, but no mention is made of the gas content of the alloys. The metals were melted under hydrogen, but how far can dissolved hydrogen affect the equilibrium conditions? In the region of Fe_3Al a mysterious additional face-centred cubic phase-structure appears in the X-ray powder photographs, with a spacing identical to that of Fe_4N. This is almost certainly formed from the residual nitrogen present in the virgin metals, which, as it does not appear in the normal spectrographic or chemical analyses, might be overlooked. I am tempted to ask how far the presence of absorbed gases influences the equilibrium, and if the nitrogen has as great an effect as carbon in steels. I must add that a careful microscopic study of Fe_3Al has failed to reveal the presence of Fe_4N when the X-ray diffraction patterns have disclosed quite an appreciable amount of it.

I was particularly interested in the region $\alpha + \alpha' + \beta$, which has been established from the micrographic study, and which was not shown by the early X-ray work. It is probable that the complex nature of this region was not revealed, partly because of the insufficient number of alloys which were examined in the earlier work, and partly because of the possibility of the α and α′ phases developing equal lattice parameters, which, from the insufficient X-ray data, would suggest that α and α′ joined together, whereas, in fact, they retain their identities at all temperature levels. This problem of equal lattice parameters is very important when dealing with polynary systems. The phenomenon was first observed in the binary Ni–Al system when, at 1100° C., the lattice parameters of the α and α′ phases become equal, and also in the $\beta + \beta'$ region of the Fe–Ni–Al system. The same thing occurred in the $\alpha + \alpha'$ region of the system Cu–Ni–Al and doubtless will be found to occur quite frequently in quaternary and higher polynary systems where the number of degrees of freedom is greater. In fact, the equality of spacings will tend to lessen the strain between co-existing phases and the phase boundaries will tend to adjust themselves accordingly.

This principle of least strain or equivalence of interatomic distances (or principle of epitaxy) must take its place with the electron-atom ratio and atomic size as a factor which influences the thermodynamic potential of the system and the consequent positioning of the phase boundaries. That a two-phase alloy can consist of phases with similar structures and identical spacings makes it imperative to use the micrographic method side

by side with the X-ray technique, and the present study by Dr. Bradley illustrates, in an admirable way, the essentially complementary nature of the two methods of approach.

Finally, a publication by Schramm[16] on the Ni–Al system appeared much later than that of Alexander and Vaughan.[17] Schramm considers that Ni_3Al is formed by the peritectic reaction : liquid + $\alpha = \alpha'$ at 1362° C., whilst Alexander and Vaughan give : liquid + $\beta = \alpha'$ at 1395° C. This alternative method of formation of the α' phase will presumably necessitate a re-assessment of the equilibrium relationships in the region of the $\alpha + \alpha' + \beta$ three-phase field. It may be, however, that I am anticipating a point which is to be dealt with in the papers which are to supplement the present one.

Mr. **J. Gordon Parr** (Liverpool University) : As we are embarking upon a study of the Fe–Mn system in the Metallurgy Department of Liverpool University, the paper by Dr. Pumphrey and Dr. Jones is of great value to us : for, although our particular interest lies in the ε phase, the two projects have much in common.

Considering first the thermodynamic approach, it is interesting and reassuring to observe that equation (20) —$c_\alpha/c_\gamma = e^{-\Delta H/RT}$—may be proved directly from the Van't Hoff relation which has been derived by Wilson.[18] Despite the advantages of the method, the calculation of free-energy changes from an equilibrium diagram might be criticized as being a reversal of logical procedure, and it could possibly lead to errors which might pass undetected. Calculation by an alternative method would allow any existing equilibrium diagram to be used in corroboration. In this respect, a paper by Fisher[19] is of interest, in that an expression is derived which indicates how such free-energy calculations may be made.

It appears to be quite logical to compare the mechanism of transformation with the austenite–martensite change, but the evidence offered to dismiss the possibility of nucleation occurring is not sufficiently convincing. Indeed, I find it difficult to imagine any phase change which is not nucleated in some way. Fisher, Hollomon, and Turnbull[20] have put forward a hypothesis to explain all types of phase transformation, the basic assumption of which is that potential nuclei of phase α, of less than a critical size and so possessing no definite interface, can exist in phase γ, under conditions where the γ phase is the stable one. These potential nuclei are called embryos, and for each temperature there is a critical embryo size, above which size it will form a nucleus, and below which it will disappear. In an athermal phase change, such as the one under discussion, cooling from a temperature within the γ phase, at a rate above critical, will result in embryos being 'frozen,' so that at the quenching temperature some will be above the corresponding critical size and will form nuclei. This hypothesis, which, from the very nature of the presumed embryos, cannot be readily disproved, agrees with experimental observations of quenching and stabilization phenomena.

In the light of this, the evidence on which the authors dismiss the possibility of nucleation is not valid, and, in fact, the stabilization phenomenon they record is in direct support of the above hypothesis.

Assuming that nucleation does occur, the subsequent formation of the α phase must be accounted for, and if the transformation is considered to be of the same type as the austenite–martensite change, it may progress by a shear mechanism. There is, however, the possibility of rapid growth. This is discussed, in relation to the austenite–martensite transformation, and is put on a mathematical basis by Fisher, Holloman, and Turnbull.[21] This theory, which is claimed to be supported by experimental work, may well be extended to other systems.

I feel that, in the absence of other suggested mechanisms, and because of the similarity between the γ–α phase change in the Fe–Ni, Fe–Mn, and Fe–C systems, the possibility that this transformation is a nucleation and growth process should be seriously considered.

CORRESPONDENCE

Dr. Ing. **H. Lepp** (Paris) wrote : I should like to draw the authors' attention to the following points.

Firstly, from a fairly detailed mathematical analysis of classical thermodynamics, the authors arrive at the following equations for their calculations :

$$\Delta F_{Fe} = 4{\cdot}57 \times T_1 \times [\log_{10}(1 - c_\alpha) - \log_{10}(1 - c_\gamma)] \quad \ldots\ldots(a)$$

$$\Delta H = 4{\cdot}57 \times T_1 \times [\log_{10} c_\gamma - \log_{10} c_\alpha] \quad \ldots\ldots(b)$$

These two equations are identical, for, from consideration of the concentrations :

$$c_\alpha + c_\gamma = 1$$

there are $c_\alpha = 1 - c_\gamma$ and $c_\gamma = 1 - c_\alpha$

and $\dfrac{c_\alpha}{c_\gamma} = \dfrac{1 - c_\gamma}{1 - c_\alpha} = K$ = constant of transformation.

Hence : $-[(\log c_\alpha - \log c_\gamma)] = -[(\log (1 - c_\gamma) - \log (1 - c_\alpha)]$,

and $\log c_\gamma - \log c_\alpha = \log (1 - c_\alpha) - \log (1 - c_\gamma)$.

In other words, in the authors' calculations, everything depends upon the mathematical expression that is given to the values of the concentrations for c_α and c_γ, but unfortunately, this is often a source of error and of misunderstanding. Hence, ΔF_{Fe} and ΔH represent only the free energy of the $\alpha \rightleftharpoons \gamma$ transformation.

From the fundamental equation of thermodynamics :

$$-\Delta F = -RT \log_e K = -4{\cdot}573T \log_{10} K = -\Delta Q + \Delta ST.$$

Would it not be preferable to calculate separately this heat in ΔQ by the classical equation :

$$\Delta Q = \Delta H_0 + (\Delta a)T + \tfrac{1}{2} + (\Delta b)T^2 + \tfrac{1}{3}(\Delta c)T^3, \text{ \&c.}$$

where H_0 is the constant of integration and (Δa), (Δb), and (Δc) are to be evaluated from functions of the heat capacities and the specific heats ? The latter procedure would, at the same time, provide a check on the eventual experimental errors at the concentrations c_α and c_γ respectively.

Secondly, the authors consider that the heat of solution is independent of the temperature and of the concentration. Theoretically the heat liberated or absorbed in a process is always a function of the temperature. For the Fe–Ni and Fe–Mn systems in question their $\alpha \rightleftharpoons \gamma$ transformation curves are fairly close, but their respective solidus curves already diverge appreciably—a matter of importance from the energy viewpoint, and a possible source of error.

Further, in regard to the influence of concentration on the heat of solution, the Fe–Ni and Fe–Mn systems form a continuous series of solid solutions, and thus this influence is neither very pronounced nor serious.

On the other hand, according to my own experience and calculations, if intermetallic compounds are formed the heat of solution is markedly influenced by the concentrations of the constituents. For example, this is so in the solid-solution (α-phase) regions in the Cu–Sn system, with its exothermic intermetallic compounds such as $Cu_{31}Sn_8$ (δ phase) and Cu_3Sn (ε phase)—particularly δ phase, which precipitates easily.

To control thermodynamically the mechanism of the formation of an alloy, representation by the following general formula has been of great service to me in my calculations :

$$x\mathrm{Cu} + (1 - x)\mathrm{Sn} = \mathrm{Cu}_x\mathrm{Sn}_{(1-x)}$$

$$\text{and } \frac{\mathrm{Cu}_x\mathrm{Sn}_{(1-x)}}{(\mathrm{Cu})^x\,(\mathrm{Sn})^{(1-x)}} = K = \text{constant},$$

where x and $(1 - x)$ are the respective atomic fractions. Thus, the formation of the intermetallic compound Cu_3Sn can be represented as follows :

$$3\mathrm{Cu} + \mathrm{Sn} = \mathrm{Cu}_3\mathrm{Sn} + 8000K \text{ cal.}$$

$$\text{and } \frac{\mathrm{Cu}_3\mathrm{Sn}}{(\mathrm{Cu})^3(\mathrm{Sn})} = K.$$

I hope that the foregoing may help the authors to adjust their calculations on the free energy of the process of the $\alpha \rightleftharpoons \gamma$ transformation, so as to find the real heat of the reaction in question and the variations of the entropy.

Professor **C. Crussard** (Paris) wrote : I was interested to see that Dr. Jones and Dr. Pumphrey's results are in good agreement with a theory of the martensite transformation which I proposed a year ago,[22] to which I shall refer.

For the free energy required to initiate the α–γ transformation the authors give figures of the order of 200 cal./mol., and state that it cannot be explained by the elastic strain caused by the transformation. On the contrary, I have shown that it was of the order of magnitude to be expected from the internal stresses (shear stresses) arising around a platelet of martensite (as measured by X-rays). These internal stresses can also be predicted by calculation ; I gave only a rough approximation, but recently Dr. Nabarro has proposed to identify the shear stresses around a martensite platelet with those of a close loop of dislocation, which method leads to a good quantitative agreement.*

More precisely, the average internal stress in steels, as measured by X-rays, is about half of that deduced from the free-energy barrier. This reduction in stress is caused by plastic flow and the bunching of the martensite platelets in several crystallographic directions, in such a way as to reduce the total internal-stress energy (the latter mechanism has been proposed by Dr. Orowan[23]). The hysteresis of the reverse transformation on heating is caused by this reduction in internal stress ; when no reduction of stress has occurred, there is no appreciable hysteresis, as is the case in Fe–Mn for the ε martensite (over 12% of Mn). In α martensite, the bunching process is always present, so there is always some hysteresis. If, moreover, plastic flow occurs around the martensite platelet (or inside, if the martensite is not very hard, as in Fe–Ni), the hysteresis may be very pronounced.

At high transformation temperatures (or low Ni content), the plastic flow is so easy that relaxation of the stress may occur nearly instantaneously, and it may be very difficult to distinguish between martensite and bainite when no carbon is present, as in the case under discussion. This instantaneous relaxation explains the authors' finding that the free-energy barrier increases from 0 cal./mol. for pure iron, to 200 cal./mol. for approximately 15% of Ni (or 400° C.), owing to an increasing difficulty for the relaxation to occur. Below 400° C. the resistance to deformation (rapid) is nearly constant ; so also is the free-energy barrier.

How can the free-energy barrier be higher on heating than on cooling ? If this were true, it could be explained by the plastic deformation which accompanies the cooling transformation, so that the following heating transformation occurs in a lattice full of dislocations or other defects, which change the energy conditions ; in fact, a stabilization effect has been observed by Greninger and Mooradian[24] on brass subjected to several heating and cooling cycles through the transformation range. The position of the free-energy barrier could also be explained by developing the new theory of athermal nucleation of Fisher, Hollomon, and Turnbull,[20] although, at first glance, the transformation on heating is very difficult to explain by athermal nucleation. It may be that some inaccuracy is present in the authors' calculations.

Dehlinger[9] has given a simple way to find equations (19) and (20) of the present paper. His method allows for the variation of heat of solution with the concentration, and leads to the exact formula when the concentration is not small. This exact formula could be found by introducing a term proportional to c in equation (14) and (16) but Dehlinger and the present authors make an unjustified assumption in applying the Kopp-Neumann rule, or in assuming the heat of solution H to be independent of temperature, which is strictly equivalent. In other alloys I have proved that, by providing for small deviations from the Kopp-Neumann rule, the theoretical solubility of an alloy can be changed by a factor as high as 10.† Here, evidently, the specific heat of Ni is not the same when its co-ordination number is 8 (α state) as when it is 12 (γ state) ; moreover, the specific heat of iron is changed by the vicinity of the Ni atoms. This introduces a new constant term and a new term proportional to c in equations (6) and (13), and changes equation (18). This explains why the authors' value of ΔFe is 25% false, and why a small error is introduced in all their results.

The experiment where cooling was interrupted at 370° C., and where the martensite formation on subsequent cooling resumed only at 355° C., is a typical example of stabilization of austenite ; but it seems to differ from the stabilization observed in carbon steels, because in these steels the transformation curve is simply shifted to lower temperatures. In the experiment concerned, the transformation resumed so rapidly that the authors state that the alloy was reheated, which is impossible in a true martensite transformation. As stabilization is still a puzzle, it would be interesting to know if the new transformation curve (*i.e.*, percentage of martensite *versus* temperature) rejoined the normal one slightly below 355° C.

The abnormal point A underlined in Fig. 5, about 6% of Ni, is probably caused by the very dispersed state of the phase, which ought to be present as small particles where the martensite transformation is more difficult (particle-size effect). The abnormal point A at 30·3% of Ni, I consider, is caused by what I have called spreading of the Ms point, owing to thermal fluctuations in composition.

When an 18/8 stainless steel is transformed by cold-working, the martensite produced is tetragonal. The tetragonality is much too high to be explained by internal stresses, but it can be explained by some kind of ordered distribution (as in brass). Such behaviour can be expected from a steel containing about 25% of Ni. In fact, in the paper by Owen and Liu, faint lines of tetragonal α structure can be observed on the X-ray diagram of the alloys containing from 20 to 36% of Ni. It is very probable that this ordering is responsible for the break at 20% in the curve in Fig. 9.

Dr. **H. K. Hardy** (Fulmer Research Institute) wrote : The application of thermodynamics to problems of physical metallurgy, similar to that discussed by Jones and Pumphrey, inevitably involves difficulties in the

* Private communication.

† C. Crussard and F. Aubertin : To be published.

presentation of results. Thermodynamics and, more particularly, the method of chemical potentials are outside the scope of most degree courses in metallurgy. Authors of papers in which the thermodynamic method is employed then have the difficulty of writing for two types of reader : (i) those interested in the results ; and (ii) those interested in the method of obtaining the results. The only satisfactory way of dealing with this difficulty is probably that adopted by the authors of putting their analysis in the form of an appendix. I am going to follow this procedure by giving firstly the results, and secondly their derivation.

One advantage of using chemical potentials in the general treatment of phase equilibria is that the significance of the terms is stated at the outset and does not depend on interpretation at the end of the analysis. For instance, it is shown in the following lines that the authors' value of ΔF_{Fe} actually involves the difference between the partial molar heats of solution of iron in the γ and α phases as well as the free-energy difference between pure γ and pure α iron. The discrepancy reported by the authors for the Fe–Ni and Fe–Mn systems, and also between Zener's results and their own, can be accounted for on this basis.

The authors' expressions for the relative free energies of the α and γ phases are better written as :

$$f_\alpha = c(\overline{\Delta F}_{J_0} + \overline{\Delta H}^{\alpha-\gamma}_J) - RT\,Sp(c)$$

$$f_\gamma = (1-c)\,(\overline{\Delta F}_{Fe\alpha} + \overline{\Delta H}^{\gamma-\alpha}_{Fe}) - RT\,Sp(c)$$

instead of : $f_\alpha = c\Delta H - RT\,Sp(c)$

$$f_\gamma = (1-c)\Delta F_{Fe} - RT\,Sp(c)$$

where the meaning of these terms is given in the text that follows.

This does not, however, influence the numerical values, and their relative free-energy curves are unaffected.

To calculate the relative free-energy curves, the values of c_α and c_γ from the Owen and Sully diagram for the Fe–Ni system have been used in the last two equations in the authors' appendix. The averaged results have then been used in the equations immediately above. I am sure that the authors will agree that the agreement between the calculated and experimental boundaries in their Fig. 2 shows only the accuracy of their arithmetic. They do not intend it to be taken as a proof of the Owen and Sully diagram, but this is not clear unless the thermodynamic method is examined in detail.

By applying the same numerical calculations for values taken from the Hoselitz diagram, Fig. D (*a* and *b*) gives the relative free-energy curves at 300° C. from the boundaries in the Sully and Owen and the Hoselitz diagrams. The free-energy curves for the diagram corresponding to metastable equilibrium should be higher than those derived from the equilibrium phase diagram. The curves in Fig. *D* are correctly placed relative to one another, but there is no relation between each Figure.

Unfortunately, the factor connecting Fig. *D* cannot be evaluated. The relationship is given by :

$$f_\alpha = c(\overline{\Delta F}_{J_0} + \overline{\Delta H}^{\alpha-\gamma}_J) - RT\,S_p(c)$$

$$f_\gamma = (1-c)\,(\overline{\Delta F}_{Fe\alpha} + \overline{\Delta H}^{\gamma-\alpha}_{Fe}) - RT\,Sp(c)$$

$$f_\alpha[RH] = c(\overline{\Delta F}_{J_0} + \overline{\Delta H}^{\alpha-\gamma}_J)[H] - RT\,Sp(c) + cK_3 + (1-c)K_4$$

$$f_\gamma[RH] = (1-c)\,(\overline{\Delta F}_{Fe\alpha} + \overline{\Delta H}^{\gamma-\alpha}_{Fe})[H] - RT\,Sp(c) + cK_2 + (1-c)K_4$$

where $[RH]$ signifies the Hoselitz value relative to the Owen and Sully value.

The meaning of K_3 and K_4 is explained later, but this

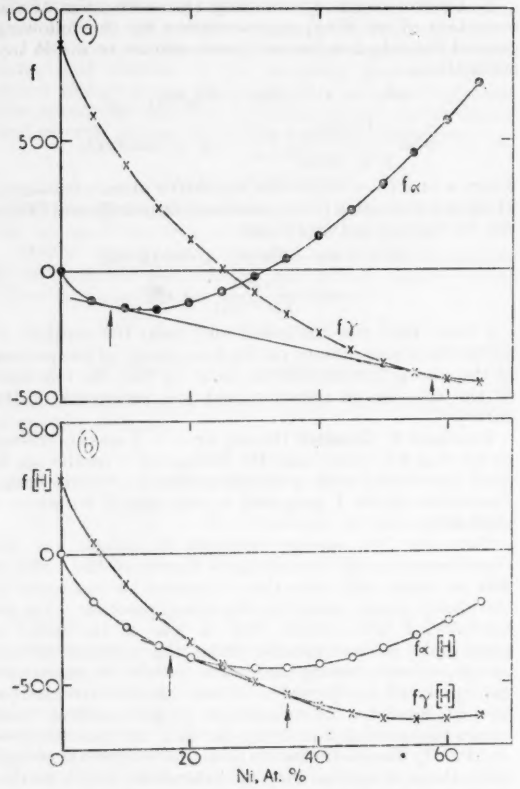


Fig. D—Relative free-energy curves ; (*a*) from the Fe–Ni phase diagram of Owen and Sully at 300° C., and (*b*) from the Fe–Ni diagram of Hoselitz

method cannot be used to decide which of the alternative diagrams is closer to equilibrium.

The general type of treatment, where the partial molar heats of solution have been assumed independent of composition, produces relative free-energy curves convex to the composition axis. It is more reasonable to assume that the curves contain both concave and convex regions within a single phase. A major difficulty in any quantitative thermodynamic approach to problems in physical metallurgy is always lack of knowledge of the activity coefficients, from which the heats of solution are derived. Attempts have been made to overcome this difficulty but it will always exist until experimental values of the activity are available.

The following paragraphs show the derivation of the results already given.

The assumptions in the authors' method are shown more clearly by deriving their ΔF_{Fe} and ΔH directly from the partial molar free energies of the components Fe and *J* in the α and γ phases.

The free energy per gram atom, *i.e.*, the chemical potentials of a component in a regular solution is given by :

$$\bar{F}^1_A = F^1_{A_0} + RTlna^1_A = F^1_{A_0} + RTlnc^1_A + RTlnf^1_A$$

where $\bar{F}^1_A$ is the chemical potential of the component *A* in phase 1, $F^1_{A_0}$ is the chemical potential of pure *A* in the standard state corresponding to phase 1 (*i.e.*, in which the activity coefficient is arbitrarily placed as

unity), a_A^1 is the activity and c_A^1 is the atomic fraction of component A in phase 1; f_A^1 is the activity coefficient at composition c_A^1.

The heat of solution $\overline{\Delta H}_A^1$ of 1 gram atom of A in the solution of composition c_A^1 is given by:

$$\overline{\Delta H}_A^1 = \overline{H}_A^1 - H_A^o = RTlnf_A^1 + RTI$$

where $\overline{H}_A^1$ and H_A^o are the heat contents of 1 gram atom of component A in phase 1 and in its standard state. I is an integration constant. This constant will be neglected in accordance with the assumption of a regular solution, and, to a first approximation, the chemical potentials of Fe and J in the α and γ phases are given by the following equations:

$$\overline{F}_{Fe}^{\alpha} = \overline{F}_{Feo}^{\alpha} + RTln(1 - c_\alpha) + \overline{\Delta H}_{Fe}^{\alpha} \quad \ldots\ldots(1)$$

$$F_J^{\alpha} = F_{Jo}^{\alpha} + RTlnc_\alpha + \overline{\Delta H}_J^{\alpha} \quad \ldots\ldots(2)$$

$$\overline{F}_{Fe}^{\gamma} = \overline{F}_{Feo}^{\gamma} + RTln(1 - c_\gamma) + \overline{\Delta H}_{Fe}^{\gamma} \quad \ldots\ldots(3)$$

$$\overline{F}_J^{\gamma} = F_{Jo}^{\gamma} + RTlnc_\gamma + \overline{\Delta H}_J^{\gamma} \quad \ldots\ldots(4)$$

The approximation involved in putting the heats of solution directly into these equations is small compared with subsequent assumptions.

The difference between the chemical potentials of the components in the two phases can now be written directly from equations (1) and (3), and:

$$\overline{F}_{Fe}^{\gamma-\alpha} = \overline{F}_{Fe}^{\gamma} - \overline{F}_{Fe}^{\alpha} = \overline{F}_{Feo}^{\gamma} - \overline{F}_{Feo}^{\alpha} + RT[ln(1 - c_\gamma) - ln(1 - c_\alpha)] + \overline{\Delta H}_{Fe}^{\gamma} - \overline{\Delta H}_{Fe}^{\alpha} \ldots (5)$$

$$\overline{F}^{\alpha-\gamma}_J = \overline{F}_J^{\alpha} - \overline{F}_J^{\gamma} = F_{Jo}^{\alpha} - F_{Jo}^{\gamma} + RT(lnc_\alpha - lnc_\gamma) + \overline{\Delta H}_J^{\alpha} - \overline{\Delta H}_J^{\gamma} \ldots(6)$$

when the authors' terminology of going from $\gamma \rightarrow \alpha$ in the first case and $\alpha \rightarrow \gamma$ in the second has been followed for more convenient comparison with their equations.

At equilibrium, equations (5) and (6) are both zero, so that the following values can be obtained:

$$RT[ln(1 - c_\alpha) - ln(1 - c_\gamma)] = \overline{\Delta F}_{Feo} + \overline{\Delta H}^{\gamma-\alpha}_{Fe} \equiv \Delta F_{Fe}$$
(of Jones and Pumphrey) ...(7)

$$RT(lnc_\gamma - lnc_\alpha) = \overline{\Delta F}_{Jo} + \overline{\Delta H}^{\alpha-\gamma}_J \equiv \Delta H$$
(of Jones and Pumphrey) ...(8)

where $\overline{\Delta F}_{Feo} = \overline{F}_{Feo}^{\gamma} - \overline{F}_{Feo}^{\alpha}$ and $\overline{\Delta F}_{Jo} = F_{Jo}^{\alpha} - F_{Jo}^{\gamma}$

$\overline{\Delta H}^{\gamma-\alpha}_{Fe} = \overline{\Delta H}^{\gamma}_{Fe} - \overline{\Delta H}^{\alpha}_{Fe}$ and $\overline{\Delta H}^{\alpha-\gamma}_J = \overline{\Delta H}^{\alpha}_J - \overline{\Delta H}^{\gamma}_J$

Thus, the authors' calculated values for ΔF_{Fe} and ΔH are shown to involve differences in the chemical potentials of the pure components in the standard states corresponding to the two phases and differences in the partial molar heats of solution.* This will account for the discrepancy they observed between the values in the Fe–Ni and Fe–Mn systems, and also the difference from Zeners calculated results for $\overline{F}_{Feo}^{\gamma} - \overline{F}_{Feo}^{\alpha}$.

The equations for f_α and f_γ can also be obtained directly from equations (1) to (4). Equating c_α to c_γ leads to:

$$F_\alpha = (1 - c)\overline{F}_{Fe}^{\alpha} + c\overline{F}_J^{\alpha} = (1 - c)\overline{F}_{Feo}^{\alpha} + c\overline{F}_{Jo}^{\alpha} + (1 - c)\overline{\Delta H}_{Fe}^{\alpha} + c\overline{\Delta H}_J^{\alpha} - RT\,Sp(c) \quad \ldots(10)$$

$$F_\gamma = (1 - c)\overline{F}_{Fe}^{\gamma} + c\overline{F}_J^{\gamma} = (1 - c)\overline{F}_{Feo}^{\gamma} + cF_{Jo}^{\gamma} + (1 - c)\overline{\Delta H}_{Fe}^{\gamma} + c\overline{\Delta H}_J^{\gamma} - RT\,Sp(c) \quad \ldots(11)$$

where $Sp(c)$ is the positional entropy at composition c.

The terms which are linear in relation to composition may be added or subtracted from both equations without altering the relative free energies. A suitable choice of this procedure leads to:

$$f_\alpha = c(\overline{\Delta F}_{Jo} + \overline{\Delta H}^{\alpha-\gamma}_J) - RT\,Sp(c) \quad \ldots\ldots(12)$$

$$f_\gamma = (1 - c)(\overline{\Delta F}_{Feo} + \overline{\Delta H}^{\gamma-\alpha}_{Fe}) - RT\,Sp(c) \ldots(13)$$

These equations now possess a homogeneous form which is lacking from the authors' corresponding equations (12) and (13). The correction, however, is one of nomenclature only, and their numerical values and the curves in their Fig. 4 are not affected.

Note that it has been assumed that $\overline{\Delta H}^{\alpha-\gamma}_J$ and $\overline{\Delta H}^{\gamma-\alpha}_{Fe}$ are completely independent of composition at any given temperature. This constitutes a major weakness and will be discussed later.

The authors used equations (12) and (13) for deriving the relative free-energy curves from the Owen and Sully diagram for the Fe–Ni phase system. It is of interest to apply this treatment to the Hoselitz diagram, in which case equations (12) and (13) can be re-written as:

$$f_\alpha[H] = c(\overline{\Delta F}_{Jo} + \overline{\Delta H}^{\alpha-\gamma}_J)[H] - RT\,Sp(c) \quad \ldots\ldots(14)$$

$$f_\gamma[H] = (1 - c)(\overline{\Delta F}_{Feo} + \overline{\Delta H}^{\gamma-\alpha}_{Fe})[H] - RT\,Sp(c) \quad (15)$$

where $[H]$ signifies a value applying to, or derived from, the Hoselitz diagram.

Although the free-energy curves obtained from equations (12) and (13) and from equations (14) and (15) are relative to one another, no comparison can be made between f_α and $f_\alpha[H]$ or f_γ and $f_\gamma[H]$.

To make this assessment it is necessary to write equations (10) and (11) in terms of Hoselitz values:

$$F_\alpha[H] = (1 - c)\overline{F}_{Feo}^{\alpha}[H] + c\overline{F}_{Jo}^{\alpha}[H] + (1 - c)\overline{\Delta H}_{Fe}^{\alpha}[H] + c\overline{\Delta H}_J^{\alpha}[H] - RT\,Sp(c) \quad \ldots(16)$$

$$F_\gamma[H] = (1 - c)\overline{F}_{Feo}^{\gamma}[H] + c\overline{F}_{Jo}^{\gamma}[H] + (1 - c)\overline{\Delta H}_{Fe}^{\gamma}[H] + c\overline{\Delta H}_J^{\gamma}[H] - RT\,Sp(c) \quad \ldots(17)$$

Relative values can now be obtained by subtracting the terms which have been placed linear with composition simultaneously from equations (10), (11), (16), and (17). A suitable procedure leads to:

$$f_\alpha = c(\overline{\Delta F}_{Jo} + \overline{\Delta H}^{\alpha-\gamma}_J) - RT\,Sp(c) \quad \ldots\ldots(12)$$

$$f_\gamma = (1 - c)(\overline{\Delta F}_{Feo} + \overline{\Delta H}^{\gamma-\alpha}_{Fe}) - RT\,Sp(c) \ldots(13)$$

$$f_\alpha[RH] = c(\overline{\Delta F}_{Jo} + \overline{\Delta H}^{\alpha-\gamma}_J)[H] - RT\,Sp(c) + c(K_1 + K_2) + (1 - c)(K_3 + K_4) \ldots(18)$$

$$f_\gamma[RH] = (1 - c)(\overline{\Delta F}_{Feo} + \overline{\Delta H}^{\gamma-\alpha}_{Fe})[H] - RT\,Sp(c) + c(K_1 + K_2) + (1 - c)(K_3 + K_4) \ldots(19)$$

where $[RH]$ signifies a Hoselitz value relative to an Owen and Sully value, and

$$K_1 = \overline{F}_{Jo}^{\gamma}[H] - \overline{F}_{Jo}^{\gamma} = 0 \quad \ldots\ldots(20)$$

$$K_2 = \overline{\Delta H}_J^{\gamma}[H] - \overline{\Delta H}_J^{\gamma} \quad \ldots\ldots(21)$$

$$K_3 = \overline{F}_{Feo}^{\alpha}[H] - \overline{F}_{Fe}^{\alpha} = 0 \quad \ldots\ldots(22)$$

$$K_4 = \overline{\Delta H}_{Fe}^{\alpha}[H] - \overline{\Delta H}_{Fe}^{\alpha} \quad \ldots\ldots(23)$$

These terms cannot be evaluated from the phase diagram. All that can be said is that the shift to be given to the curves in Fig. E is linear in relation to

---

* The significance of $ln(1 - c_\alpha) \pm ln(1 - c_\gamma)$ can also be approached by deriving the standard equation for the reduction of melting point from equation (5). This leads to $R\dfrac{\delta ln\frac{(1 - c_\gamma)}{(1 - c_\alpha)}}{\delta\left(\frac{1}{T}\right)} = H_{Fe}^{\gamma} - H_{Fe}^{\alpha}$, but equations (7) and (8) are more suitable for the subsequent treatment.

composition. This type of thermodynamic analysis based on the phase diagrams cannot be used to decide whether the Owen and Sully or Hoselitz diagrams are closer to true equilibrium conditions.

It is incorrect to assume, as in all the foregoing treatment, that ΔH_A^1, the partial molar heat of solution, is independent of composition at any particular temperature. It is this assumption which makes the relative free-energy curves always convex to the abscissa. In practice both convex and concave regions are to be expected within a single phase.[25, 26, 27] Any quantitative or semi-quantitative approach to problems in physical metallurgy is greatly hindered unless the activity coefficients are known or can be allowed for in the analysis.[28, 29]

Dr. **K. Hoselitz** (Permanent Magnet Association) in a further contribution wrote : Dr. Sully has referred to a possible explanation for the discrepancies between the phase boundaries arrived at in the present paper and by Hoselitz and Sucksmith.[2] He infers that, in our work, a metastable state was reached, and he attempts to explain the existence of this metastable state on the basis of the inversion point of the free-energy curve, owing to the existence of a Fe_3Ni super-lattice in the γ state. Consequently, at 33–35% of nickel the second differential coefficient of the free energy, $\delta^2F/\delta c^2$, would become zero, and nucleation would be favoured at this composition.

If closer inspection of the actual experimental condition is attempted some doubt is thrown on Dr. Sully's remarks. Although it is known that, at compositions where $\delta^2F/\delta c^2 = 0$, nucleation during changes in composition is likely to take place, this is not the case if there is a phase change from one lattice form to another. Therefore, it would be more likely that nucleation of a metastable state had occurred if alloys initially in the γ state were treated at a temperature of, say, 400° C. when, instead of changing to the equilibrium composition, one might have found an intermediate γ phase in the form of nuclei at a second composition where the second differential is zero. Starting with an alloy in the α configuration, produced by quenching in liquid air, the final equilibrium composition of γ would be precipitated, and the fact that, at some point between the composition of the actual alloy and the composition of the equilibrium γ phase, the second differential of the free energy of the γ phase became zero would not be relevant. These circumstances are fully explained and treated by Cottrell.[30]

The existence of a super-lattice in the γ phase at the composition Fe_3Ni has clearly been indicated by the magnetic work of Hoselitz.[3] In fact, if a super-lattice were to be found in the γ phase at the composition FeNi, Dr. Sully's attempted explanation of the possible occurrence of a metastable state could apply to the γ–phase determination in the present authors' paper.

There is, however, a further reason why Dr. Sully's hypothesis is not likely to be applicable in this case. The second differential coefficient is important for the composition at which nuclei are formed. I think it is clear that as precipitation proceeds, and larger and larger quantities of the equilibrium phases appear, the composition of the nuclei must change from one where $\delta^2F/\delta c^2 = 0$ to the equilibrium composition. Sully has quoted times of approximately 90 and 180 days, between which he noticed a change in the sharpness of the X-ray lines, the sharp lines appearing after 180 days. I would again like to draw his attention to the fact that our alloys were annealed for 150 days, *i.e.*, for about the same length of time as Dr. Sully's longer time ; after that the measured amount of γ phase in some of our alloys had reached 60%. There can be no question that the early state, where nucleation is important, has long been passed.

Mr. **F. J. Shortsleeve** (Standard Oil Company (Indiana) Chicago, U.S.A.) wrote : In regard to the paper by Mr. Rees, Mr. Burns, and Mr. Cook, during the past two years the Engineering Research Department of Standard Oil Company (Indiana) has investigated the salient features of σ formation in Cr and Cr–Ni stainless steels. The steels studied contained from 0·28 to 0·89% of Si, 0·33 to 0·86% of Mn, less than 0·1% of C, approximately 0·025% of S, and approximately 0·025% of P.

The location of the $\alpha/\alpha + \sigma$-phase boundary was determined for Cr steels, using powder samples (170-mesh filings) containing between 15 and 30% of Cr. The powder method of X-ray diffraction was used for constituent identification. An X-ray diffraction determination was also made of the phases present in powder samples (170-mesh filings) of several Cr–Ni steels (containing from 15 to 30% of Cr and 0 to 20% of Ni), which had been annealed for 1900 hr. at 1200° F. (649° C.). This permitted drawing the probable limits of the regions of σ stability for these ternary steels.

A comparison of our results was made with the Fe–Cr diagram of Dr. Jones and Mr. Cook and the Fe–Cr–Ni diagram of Mr. Rees, Mr. Burns, and Mr. Cook, It appears that a normal amount of steelmaking impurities displaces the $\alpha/\alpha + \sigma$-phase boundary of the Fe–Cr system to lower values of Cr. The maximum effect occurs at 1100° F. (593° C.)—the lowest temperature studied—where the boundary is displaced by about 6% of Cr.

In the ternary alloys, the $\alpha/\alpha + \sigma$-phase boundaries of the two diagrams, drawn for 1200° F. (649° C.), are roughly parallel, and are displaced from one another by about 5% of Cr. The α triple point of the three-phase ($\alpha + \gamma + \sigma$) triangle lies at approximately $2\frac{1}{2}$% of Ni and 16% of Cr for our Cr–Ni steels, compared with about $1\frac{1}{2}$% of Ni and 24% of Cr for their high-purity alloys. Within the limits of experimental accuracy, the γ triple points of both diagrams are nearly the same, and the $\gamma/\gamma + \sigma$-phase boundaries are identical.

It appears that, although the steelmaking impurities usually found in commercial alloys displace the $\alpha/\alpha + \sigma$-phase boundary to lower values of Cr, they have very little effect on the location of the $\gamma/\gamma + \sigma$-phase boundary. In other words, the solubility of Cr in the α phase is decreased by the steelmaking impurities, but the solubility of Cr in the γ phase remains practically unchanged.

REFERENCES

1. E. A. Owen and A. H. Sully : *Philosophical Magazine*, 1939, vol. 27, p. 614.
2. K. Hoselitz and W. Sucksmith : *Proceedings of the Royal Society*, 1943, vol. 181, Series A, p. 303.
3. K. Hoselitz : *Journal of The Iron and Steel Institute*, 1944, No. I, p. 193P.
4. A. T. Pickles and W. Sucksmith : *Proceedings of the Royal Society*, 1940, vol. 175, Series A, p. 331.
5. W. J. Barnett, *Metal Progress*, 1948, vol. 53, No. 3, p. 366.
6. E. A. Owen and A. H. Sully : *Philosophical Magazine*, 1939, vol. 27, p. 614.
7. E. A. Owen and A. H. Sully : *Ibid.*, 1941, vol. 31, p. 314.
8. F. C. Nix, H. G. Beyer, and J. R. Dunning : *Physics Review*, 1940, vol. 58, p. 1031.
9. O. Dehlinger : "Physical Chemistry of Metal Alloys," Leipzig, 1939 : Akad. Verlag.
10. G. Borelius : *Annales de Physik*, 1938, vol. 33, p. 517.
11. L. S. Darken : *Transactions of the American Institution of Mining and Metallurgical Engineering*, 1946, vol. 167, p. 546.
12. "Basic Open-Hearth Steelmaking," p. 480, New York, 1944 : American Institute of Mining and Metallurgical Engineers.

13. O. KUBASCHEWSKI and O. VON GOLDBECK : *Transactions of the Faraday Society*, 1949, vol. 45, p. 948.
14. G. GRUBE and M. FLAD : *Zeitschrift für Elektrochemie und Angewandte physikalische Chemie*, 1942, vol. 48, p. 377.
15. A. J. ZUITHOFF : *Recueil des Travaux Chimiques des Pays-Bas*, 1940, vol. 59, p. 131.
16. J. SCHRAMM : *Zeitschrift für Metallkunde*, 1941, vol. 10, p. 347.
17. W. O. ALEXANDER and N. B. VAUGHAN : *Journal of the Institute of Metals*, 1937, vol. 61, p. 247.
18. A. J. C. WILSON : *Journal of the Institute of Metals*, 1944, vol. 70, p. 543.
19. J. C. FISHER : *Journal of Metals*, 1949, vol. 185, p. 688.
20. J. C. FISHER, J. H. HOLLOMON, and D. TURNBULL : *Journal of Applied Physics*, 1948, vol. 19, p. 775.
21. J. C. FISHER, J. H. HOLLOMON, and D. TURNBULL : *Journal of Metals*, 1949, vol. 185, p. 691.
22. C. CRUSSARD : *Symposium on Metal Physics* (Conservatoire National des Arts et Métiers), 1948, pp. 39–53, I.R.S.I.D.
23. E. OROWAN : *Symposium on Internal Stresses in Metals and Alloys*. Monograph and Report Series, No. 5, 1947, The Institute of Metals.
24. A. B. GRENINGER and V. G. MOORADIAN : *Transactions of the American Institute of Mining and Metallurgical Engineers*, 1938, vol. 128, pp. 337–368.
25. R. BECKER : *Zeitschrift für Metallkunde*, 1937, vol. 29, No. 8, p. 245.
26. J. C. SLATER : " Introduction to Chemical Physics," New York, 1939 : McGraw-Hill.
27. H. K. HARDY : *Journal of the Institute of Metals*, 1950, vol. 77, pp. 457–488.
28. G. BORELIUS, F. LARRIS, and E. OHLSSON : Arkiv for Matematik, Astronomi och Fysik, 1944, vol. 31A, No. 10.
29. G. BORELIUS : *Ibid.*, 1945, vol. 32, No. 1.
30. A. H. COTTRELL : " Theoretical Structural Metallurgy," p. 225, London, 1948 : Edward Arnold.

AUTHORS' REPLIES

Professor **Owen** and Dr. **Liu** : Dr. Hoselitz states that a combination of cold-work at one temperature with heat-treatment at another might cause complex conditions that would not necessarily be helpful in securing equilibrium conditions. He also considers that the annealing times between the cold-working operations are too short. The experimental results, and the conditions under which they were obtained, invalidate these criticisms. For instance, the results obtained with lump specimens of alloys in the critical range at 400° C. agree with the results obtained with powder specimens of the same alloys taken from another part of the original ingot, these specimens having been annealed for about 18 weeks at 400° C., when 6 weeks would have sufficed to produce equilibrium according to Hoselitz's own calculations. It is most unlikely that there should be this agreement between the two investigations if Hoselitz's contention were correct.

The existence of a metastable state has been suggested to explain the difference between the present results and those of Sucksmith and Hoselitz. The vital consideration as regards location of the phase boundaries is whether the regions between the curves recorded in the two investigations, say at 400° C., contain a mixture of phases or a single phase. We find duplex phases in these regions in both of our investigations. The question of the existence of the metastable state is now under investigation in this laboratory, but no definite conclusions have yet been reached. Further discussion on this point must await the results of experiment.

Dr. Hoselitz mentions that he and his collaborators can repeat their results, but this is no proof that they are the correct results or that the interpretation of the results is correct. There is no difficulty in detecting the second phase by the X-ray method. In the determination of the $(\alpha + \gamma)/\gamma$ boundary, for instance, the (110) diffraction line of the α structure is very intense and persists in the spectra if only small amounts of the α phase (about 0·5 at.%) are present ; there is no mistaking it. Neither can we accept the suggestion that fluctuations in composition account for the differences observed, because many samples were examined from different parts of the ingot, and all gave the same result.

It is gratifying to find that the results of Dr. Kubaschewski, of the National Physical Laboratory, obtained by the thermo-chemical method and quite independently of any phase-boundary data, agree so closely with our own. This independent evidence goes a long way to establish the correctness of the equilibrium diagram that we have proposed from this laboratory.

Dr. Sully has dealt with the possible explanation of the difference observed in the position of the γ boundary in the different investigations. His main argument appears to us to be feasible. We are of the opinion, however, that further experiment is needed before an attempt is made to explain the differences in detail.

Dr. **F. W. Jones** wrote in reply : Both Dr. Raynor and Dr. Hardy have commented that Fig. 2 of our paper, in which we compared the calculated Fe–Ni phase diagram with Owen's phase diagram, merely shows that our arithmetic was accurate. In equations (18) and (20) of our paper, there are two parameters, ΔF_{Fe} and ΔH. Obviously, at any one temperature it is possible to choose values of these parameters which give the observed concentrations c_α and c_γ. In fact, we assumed that the parameter ΔH, was independent of temperature. It would be expected to be roughly constant, and, as nothing is known of the way it depends on temperature, it appeared simpler to assume that it was constant rather than to introduce quite arbitrary temperature variations into ΔH to get exact agreement between calculated and observed phase diagrams. It was, therefore, interesting to compare the observed and calculated diagrams. The agreement is not exact, but it is sufficiently good to justify some confidence in the free-energy relationships. If we had been quite unrestricted in the values assigned to ΔF_{Fe} and ΔH, then exact agreement would have been merely a matter of accurate arithmetic, but the main object of the paper was to interpret the diffusionless transformations in terms of the equilibrium diagram by means of the free-energy curves.

In reply to Dr. Raynor on the effect of cold-work, we believe that it has been shown that cold-work facilitates the transformation $\gamma \rightarrow \alpha$ in iron–nickel alloys. The effect is well known in austenitic steels of the 18/8 type.

Dr. Allen suggests that the resistance to transformation cannot be a simple mechanical resistance to shear, since it is as great at 600° C., when the alloy is soft, as at 200° C., when the alloy is hard. 'Soft' and 'hard' refer to the properties of the bulk material, which, of course, vary with temperature ; the interatomic binding forces are almost constant. While the mechanism of the lattice change face-centred cubic $\rightleftharpoons$ body centred is obscure, it certainly differs from the deformation of bulk material by simple shear, and we consider that it is unlikely that the resistance to the lattice change is determined by the resistance of the bulk material to plastic deformation.

It is satisfactory to learn that Dr. Kubaschewski's free energies, obtained by quite a different method, are in reasonable agreement with those derived by us from the phase diagram. The point about the validity of the Neumann-Kopp rule is interesting in view of the remarks of Professor Crussard.

Mr. Parr seems to have missed our point about nucleation. In some transformations, usually where diffusion is concerned, the transformation is held up by the difficulty of formation of stable nuclei of the precipitating phase, arising from the surface energy of the interphase boundaries. We showed that in a 14·6% Ni alloy, the $\alpha \rightarrow \gamma$ transformation was not facilitated by the presence of some of the γ phase. We agree that it is probable, in Fe–Ni alloys, that the transformation starts from nuclei of some kind, but not that the difficulty of nucleus formation is the factor which determines whether or not the transformation shall take place.

In reply to Dr. Lepp, the sum of c_α (the nickel concentration in the α phase) and c_γ (the nickel concentration in the γ phase) is not unity.

We note that Professor Crussard disagrees with our suggestion that the hysteresis between the $\gamma \rightarrow \alpha$ and $\alpha \rightarrow \gamma$ transformations is caused by an energy barrier, rather than by strain energy stored in the material. According to our calculations, the strain energy associated with the volume changes was 10–20 cal./g./atom, *i.e.*, too small, by a factor of between 10 and 20, to account for the observed hysteresis. We shall be interested to see Professor Crussard's calculations, and those of Dr. Nabarro, when they become available. It is possible that thermal measurements might be helpful in the question of the amount of elastic energy stored in the alloy.

In conclusion we would draw attention to a paper by Cohen,* whose theory of the austenite–martensite transformation in steel is very similar to our treatment of the diffusionless transformations in iron–nickel alloys.

Dr. **A. J. Bradley** wrote in reply : Dr. G. V. Raynor has remarked on a number of points arising from this work, which are very important. The phase rule has been employed in order to construct the isothermals, and a separate account will be given of any instances when the micrographs seriously infringe this. Too much concern should not be shown about the detailed accuracy of the present work, especially as the scale of the isothermals is too small to show the finer details.

There is no question of any β alloy being included in the $\beta + \beta'$ field at 1150° C., but this cannot be seen very clearly from Fig. 35. Vertical sections, which will be reproduced later, clearly indicate these facts. Later work will also include representative photographs of alloys from the $\beta + \beta'$ and $\alpha + \beta + \beta'$ phase fields. Although no $\beta + \beta'$ alloy was found at 1150° C., it is certain that it must occur at this temperature, since otherwise there could be no $\alpha + \beta + \beta'$ phase field.

There is no evidence of $\beta + \beta'$ alloys between 1150 and 1350° C., and a far more detailed investigation is required to test this. The point of junction of the ordered and disordered phases cannot easily be studied by the microscope, because the microsections of β and β' phases are too similar in appearance ; hence the β–β' boundary can only be checked when one of the selected points (at intervals of 2½% in the present investigation) happens to coincide with a two-phase $\beta + \beta'$ alloy. This problem is always likely to occur when two phases are as similar as the β and β'.

On the contrary, the two-phase $\beta + \beta'$ region cannot itself be safely identified by means of X-rays, because the lines of the two phases are almost bound to overlap when their compositions are so similar. For this reason a high-temperature X-ray investigation, although very desirable on other grounds, is quite as likely to lead to ambiguous results. A possible problem for future investigation is the line of junction of the two-phase $\beta + \beta'$ region with the composition Fe_3Al, since this also lies at the boundary of the disordered β alloys and the ordered β' alloys, but, as Dr. Taylor has pointed out, this problem is itself complicated by the mysterious appearance of an ' extra ' phase at compositions near to Fe_3Al. For this reason no further work on the ternary alloy was carried out in the present investigation.

Dr. Taylor suggests that the face-centred cubic phase, which sometimes occurs mixed with Fe_3Al, is caused entirely by the presence of gaseous impurities. This may be so, and it is interesting that Dr. Goldschmidt and the author† found similar difficulty with Fe–Cu–Al alloys. The similarity to Fe_4N is suggestive, but whether nitrogen is present in these alloys, I could not say. The gases were pumped off while the alloys were still molten, so that it seems difficult to understand why any should remain after solidification.

I am glad that Dr. Taylor has referred to the $\alpha + \alpha' + \beta$ alloys, since these present perhaps the most interesting problem of all. Another paper is being written to show how these alloys differ from the $\alpha + \beta + \beta'$ alloys. They are more difficult to study, since the X-ray powder photographs give no hint of the problem. The α and α' phases are difficult to distinguish. The tie lines swing round until the lattice spacings are equal, and no person would ever suspect them of being two different phases ; the micrographs, unfortunately, confirm this conclusion. There is no sign of any three-phase effect, even after considerable periods of etching. The appearance of a typical $\alpha + \alpha' + \beta'$ alloy corresponds to that of a two-phase $\alpha' + \beta'$ alloy. In a few seconds the α and β' phases are clearly distinguishable under quite a low magnification. Some time and very thorough etching are required to reveal any difference whatever between the α and α' phases. Even then magnifications of $\times$ 1000 up to $\times$ 4000 are required.‡

Mr. **W. P. Rees** wrote in reply : Dr. Raynor has spoken of the very pronounced acceleration of the rate of reaction in the alloys by cold-work before annealing, but he appears to suspect the factor of 6×10^3 quoted on p. 333. This figure was, of course, obtained from the data tabulated on the same page, which give, more quantitatively, the observations made during the course of the work ; namely, that the reactions at 650° C. can be exceedingly sluggish ; consequently, the utmost precautions were necessary to ensure that equilibrium had been attained. His suggestion that there may be a tendency for σ phase to form in the Cr–Ni system is interesting ; this possibility had been recognized, but no clear evidence of it had been obtained.

Dr. Andrews rightly emphasizes the difficulty of detecting small traces of σ. X-ray examination of electrolytically separated residues has since been used at the National Physical Laboratory, and has led to some interesting results, which will be reported later to the Institute. His remarks about the apparent discrepancies in the amounts of α and α_2, found by X-ray and microscopic methods, are not entirely clear. If the γ-solid solution, in the presence of α, transforms on cooling to α_2 the ease of detection of α, either by X-ray or microscopic methods, depends on the relative amount of α present ; in general the microscopic method is more certain in deciding whether α is present.

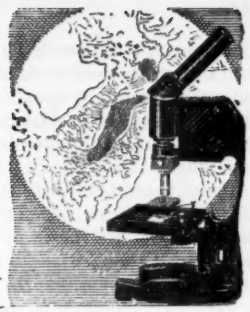
The comparison of Mr. F. T. Shortsleeve's results on commercial Fe–Ni–Cr alloys with those in the paper is interesting in indicating that the solubility of Cr in the α phase is decreased but is not affected in the γ phase.

* M. Cohen, *American Society for Metals*, 1949, vol. 41, p. 35.

† A. J. Bradley and H. J. Goldschmidt, *Journal of the Institute of Metals*, 1940, vol. 65, p. 398.

‡ A. J. Bradley, *Metal Industry*, 1950, vol. 76, No. 3, p. 49.

B. I. S. R. A.



BRITISH IRON AND STEEL RESEARCH ASSOCIATION

The Thermodynamics of Substances of Interest in Iron and Steel Making

By F. D. Richardson, J. H. E. Jeffes, and G. Withers

II—COMPOUNDS BETWEEN OXIDES

SYNOPSIS

A survey is made of the thermal and equilibrium data at present available for compounds between oxides of interest in iron and steel making. The standard free energies of formation of these compounds from their component oxides are calculated up to 2000° C., and the results are plotted on free energy/temperature diagrams. Equations and the sources of the data are given for each compound, and limits of accuracy are proposed. The standard free energies of formation vary linearly with temperature within the limits of accuracy of the data available. The application of these diagrams to slag and similar problems is discussed.

THE previous paper in this series[94] was a review of the thermodynamic data relating to oxides of interest in iron and steel making. The present paper presents a survey of similar data relating to the compounds which can be formed between such oxides. The results should find application in iron and steel making processes and particularly in the chemical problems encountered with slags and sinters.

The data used are derived mainly from measurements of heats of formation and of heat capacities, the free energies of formation being calculated by application of the heat theorem. The diagrammatic method of presenting the data is similar to that adopted previously. The sources of data are again summarized in an Appendix, which also gives the equations recommended for ΔG° and their estimated accuracies.

HEATS OF FORMATION

Most of the heats of formation used in this paper have been determined by heat of solution or heat of combustion calorimetry. The results of many of the measurements are open to considerable doubt, since the heats required have often to be calculated by the addition and subtraction of much larger quantities. Older determinations, relying on heats of combustion, are rarely reliable because the products and completeness of combustion have frequently been assumed or have not been properly determined. Many heats of formation, which have been derived from heats of solution, have also been found unreliable. These normally rely on the difference between the heat of solution of the compound under study and the sum of the heats of solution of the constituent oxides. The heats of mixing of the separate solutions of the constituent oxides have frequently not been allowed for, although they may well be significant. It is also common to find that estimates have been made of other secondary and even primary heat changes which enter into the calculations, because all the necessary reactions may not be realizable by solution methods.

HEAT CONTENTS, ENTROPIES, AND FREE ENERGIES

The gram molar heat contents and entropies of the oxides and oxide compounds, for which data are available, are given in the Tables of the Appendix.

Paper SM/23/50 of the Chemistry Department of the Steelmaking Division of the British Iron and Steel Research Association, received 4th February, 1950.

* Dr. Richardson is Head of the Nuffield Research Group in Extraction Metallurgy at the Royal School of Mines; Mr. Jeffes is a member of the staff of the British Iron and Steel Research Association; and Mr. Withers is on the staff of the F.B.I. The authors were all on the staff of the Research Association when the paper was written.

Under each compound, figures are also given for the sum of the heat contents and entropies of its component oxides in the proportion of the compound. These are valuable for calculations of the standard heat and free-energy changes for reactions involving these substances above 25° C.

From these tables it will be observed that, above 25° C., the heat capacities of the compounds are nearly equal to the sum of the heat capacities of their constituent oxides. It is frequently useful to assume this equality to make rough estimates of free-energy changes at high temperatures. If the heat capacities are additive above 298° K. :

$$\Delta G^\circ_T = \Delta H^\circ_{298} - T\,\Delta S^\circ_{298} \quad \ldots\ldots\ldots\ldots (1)$$

Whether they are additive or not :

$$\begin{aligned}\Delta G^\circ_T = {} & \Delta H^\circ_{298} \\ & + [(H_T - H_{298})_{\text{cpd.}} - \Sigma (H_T - H_{298})_{\text{const. oxides}}] \\ & - T\,\Delta S^\circ_{298} \\ & - T[(S_T - S_{298})_{\text{cpd.}} - T\Sigma (S_T - S_{298})_{\text{const. oxides}}] \quad (2)\end{aligned}$$

ΔG°, ΔH°, and ΔS° are the standard free energies, heats, and entropies of formation ; H and S are the heat contents and entropies of the substances concerned in their standard states ; and T is the absolute temperature.

The most obvious set of conditions for which equations (1) and (2) will agree is that :

$$(H_T - H_{298})_{\text{cpd.}} = \Sigma\,(H_T - H_{298})_{\text{constituent oxides}} \quad \ldots (3)$$

and,

$$(S_T - S_{298})_{\text{cpd.}} = \Sigma\,(S_T - S_{298})_{\text{constituent oxides}} \quad \ldots (4)$$

Even when this is not the case, the effect of non-additivity of the heat capacities on the separate entropy and heat content terms of the ΔG° equation is such as nearly to cancel.

These points are emphasized by comparison of the values of $(H_T - H_{298})$, $(S_T - S_{298})$, and $(H_T - H_{298}) - T\,(S_T - S_{298})$, calculated from heat-capacity measurements on the compounds, with those calculated by addition of the corresponding quantities for the component oxides. The heat contents of the compounds generally lie within about 4% of the sum of the heat contents of the component oxides, both at room temperature and as far above as data exist. The entropies at room temperature, however, are not so closely additive, owing to the manner in which they are markedly influenced by small heat effects at very low temperatures. Above room temperature, the changes in entropies of the compounds $(S_T - S_{298})$ are as closely additive as the heat contents.

The difference between values of the expression $(H_T - H_{298}) - T\,(S_T - S_{298})$ for any compound, and for the sum of its component oxides, is equal to the error which would arise in the value of ΔG° if it were calculated on the assumption that the heat capacities are additive. Most of these differences, shown in the Tables of the Appendix, are less than 1 kg.cal., and considerably less than the differences between the corresponding heat content and entropy terms. Only in the cases of the borates and phosphates do these differences exceed 2 kg.cal. This is partly because of the entropy and heat changes accompanying the melting of boric oxide and the sublimation of phosphorus pentoxide. If these are excluded from the expression $(H_T - H_{298}) - (S_T - S_{298})$ the agreement is considerably better. It follows that reasonable values of ΔG°_T at high temperatures may be calculated by means of equation (1) when high-temperature heat data are lacking, provided that the appropriate heat and entropy changes are added where phase changes occur in any of the products and reactants. In many cases the error introduced into a value of ΔG° in this way, will be less than the error in the value employed for ΔH°.

HEATS OF TRANSFORMATION AND OF FUSION

Such heats of transformation and of fusion as are available, have been entered in the Tables in the Appendix. There is a shortage of reliable heats of fusion, so that it is rarely possible to extrapolate the free-energy curves into the liquid state.

Very few heats of fusion have been measured directly. Most of those quoted in the literature have been deduced from the freezing-point depressions found in phase diagrams of binary systems. They are reliable only if the solvent behaves ideally (*i.e.*, if its activity equals its molar fraction) at the lowest solute concentration at which the depression has been determined from the appropriate phase diagram. In most silicate diagrams, for example, this is normally of the order of 95–90 mol. per cent. of the solvent silica. There is no reason why the solvent should behave ideally over such a wide range, and each case needs independent substantiation before this can be assumed. Such an example is provided by wüstite, which has been shown to behave almost ideally in molten mixtures with silica between 100 and about 70% of wüstite.[93] In this case it is not surprising that the heat of fusion, which can be calculated from the binary phase diagram as 7700 cal./mole (*i.e.*, $Fe_{0\cdot95}O$), should be in close agreement with the value of about 8060 derived from different thermodynamic data by Darken and Gurry[19] for the heat of transfer of 1 gram atom of iron and of 1 gram atom of oxygen from solid to liquid wüstite. In general, however, a heat of fusion obtained from phase diagrams cannot safely be taken as more accurate than about ±25%, unless the necessary activity data are available for the solutions concerned, or unless there are other reasons for expecting the solvent to behave ideally over the necessary concentration range.

The entropies of fusion calculated from the melting points and heats of fusion, quoted in the Tables in the Appendix or by Kelley,[49] are as follows :

Compounds	Method of Determining ΔH Fusion	ΔS Fusion Per g. mole	Per g. atom*
Al_2O_3	Systems Al_2O_3–TiO_2, Al_2O_3–Al_4C_3	11·2	2·2
B_2O_3	Heat contents	7·3	1·5
FeO (in wüstite $Fe_{0\cdot95}O$†)	Equilibrium studies	5·0	2·5
MgO	System MgO–ZrO_2	6·2(?)	3·1
SiO_2	System SiO_2–Cs_2O	0·9	0·3
$MgSiO_3$†	System $CaSiO_3$–$MgSiO_3$	8·0	1·6
$CaSiO_3$	System $CaSiO_3$–$MgSiO_3$	7·4	1·5
Na_2SiO_3	Direct	9·2	1·5
	System Na_2SiO_3–$NaBO_2$	7·7	1·3
	System Na_2SiO_3–$NaAlSiO_4$	7·35	1·2
	System Na_2SiO_3–SiO_2	7·6	1·3

Compounds	Method of Determining ΔH Fusion	ΔS Fusion Per g. mole	Per g. atom*
$Na_2Si_2O_5$	System $Na_2Si_2O_5$–$NaAlSiO_4$	7·4	0·8
Li_2SiO_3	Direct	5·0	0·8
	System Li_2SiO_3–$CaSiO_3$, Li_2SiO_3–$MgSiO_3$	7·7	1·3
	System Li_2SiO_3–Na_2SiO_3	5·1	0·8
Li_4SiO_4	Direct	4·9	0·5
	System Li_4SiO_4–$ZrSiO_4$	4·2	0·5
$CaMgSi_2O_6$	System $CaMgSi_2O_6$–$KAlSi_2O_6$	10·9(?)	1·1
$CaAl_2Si_2O_8$	System $CaAl_2Si_2O_8$–$NaAlSi_3O_8$	16·1	1·2
$Ca_3B_2O_6$	Direct	20·2	1·8
$Ca_2B_2O_5$	Direct	15·2	1·7
CaB_2O_4	Direct	12·3	1·8
CaB_4O_7	Direct	21·5	1·8
$NaBO_2$	System $NaBO_2$–Na_2SiO_3	7·0	1·7
	System $NaBO_2$–$LiBO_2$	7·0	1·7
Fe_2O_4	Equilibrium studies	17·6	2·5
$FeTiO_3$	Direct	13·2	2·6

* ΔS fusion per gram molecule divided by number of atoms in molecule
† Incongruent melting point, but composition of liquid not very different from solid

From these data it is interesting to compare the four values of Na_2SiO_3, since they give an indication of the reliance which may be placed on the heat of fusion determined from phase diagrams. In the case of Na_2SiO_3, the values from phase diagrams are in close agreement—10,500 cal. (Na_2SiO_3–$NaBO_2$), 10,000 cal. (Na_2SiO_3–$NaAlSiO_4$), 10,300 cal. (Na_2SiO_3–SiO_2). Yet all three are considerably different from the more reliable directly measured value of 12,470 cal. Directly measured values are available for the heats of fusion of Li_2SiO_3 and Li_4SiO_4, but they cannot be considered reliable, as the entropy of fusion of the ortho-silicate is less than that of the meta-silicate. Similarly, it is unlikely that the entropy of fusion of $Na_2Si_2O_5$ should be less than that of Na_2SiO_3.

The value of 9·2 for the entropy of fusion of Na_2SiO_3 may be compared with values of 6·7 and 6·5 for NaCl and $NaNO_3$, both from directly measured heats of fusion.[49] It is evident that the changes taking place on the fusion of silicates are no different normally from those which accompany the melting of typical salts. The liquid silicate differs from the crystalline solid only in that it no longer possesses the long-range order peculiar to the crystal.

FREE-ENERGY DIAGRAMS

The free-energy data which have been collected, and which are cited in detail in the Appendix, are represented in Figs. 1–4, where the standard free energy of formation (ΔG°_T) is plotted against temperature. The standard states selected are the pure crystalline solids below the melting points and the pure liquids above. For the gases, which are referred to in Fig. 4, the standard state is that at 1 atm. pressure.

Breaks occur in the free-energy plots at phase-change points, the most notable appearing at the melting points. The estimated accuracy grading (*A*, *B*, *C*, or *D*) is indicated on each line.

Figure 1 shows the standard free energies of formation of silicates, and Fig. 2 the standard free energies for aluminates, spinels, ferrites, borates, etc. Figure 3 compares the free energies of formation of certain phosphates, silicates, and carbonates, the data for the carbonates being taken from Kelley.[54] Values for the dissociation constants of these compounds can be read from the diagrams by means of the logarithmic dissociation constant scale on the right-hand corner. The simplest procedure is to place a ruler on the diagram, with one edge passing through the point *D* and the point on the diagram for which the dissociation constant is required. The value of the latter is then read at the point where the ruler edge intersects the dissociation constant scale, interpolation between the figures being made on a logarithmic basis.

Figure 4 shows the standard free-energy changes for the reduction of iron from a variety of oxide compounds which can occur in ores and sinters. The equilibrium constants for these reduction reactions, which are equal to the equilibrium oxygen gas pressures when the pure phases are involved, may be read by means of the logarithmic scales drawn round the edges. These scales mark the ends of the oxygen isobars, which would cross the diagram diagonally; the oxygen pressures may be read approximately by means of a ruler and logarithmic interpolation between the scale markings.

DISCUSSION

The general nature of the diagrams is the first point of interest. The almost horizontal lines in Figs. 1 and 2 reflect the small entropy changes which accompany the formation of solid crystalline compounds from solid crystalline constituents. In contrast, pronounced upward slopes are observed for the carbonates (and phosphates above the sublimation point of phosphorus pentoxide) shown in Fig. 3, and for the reduction reactions represented in Fig. 4. These slopes reflect the large decreases in entropy which accompany the binding of an oxygen or a carbon dioxide *gas* molecule into a *solid* substance. These decreases make it possible for the iron compounds to be reduced at high temperatures, and for the carbonates to dissociate under similar conditions. Because of these decreases the carbonates are less stable than the silicates at high temperatures, although they are considerably more stable at low temperatures.

The relative stabilities of the various oxide compounds are evident from the levels of the lines in Figs. 1, 2, and 3. Since the lines do not vary greatly from the horizontal, it is possible, by plotting a tentative horizontal ΔG° curve at the ΔH° level, to make very rough estimates of the stabilities for compounds for which only the heat of formation is known.

The free-energy curves are valuable in leading to an understanding of liquid slag systems. Because of this the nature of a molten silicate melt is briefly considered. The melt must be regarded as consisting of a three-dimensional network of metal atoms and silicate groups co-ordinated with each other in many different directions. For instance, each iron atom in solid or liquid fayalite is associated with two to four silicate groups, and each silicate group with four to eight iron atoms.[93] In silicate melts there is almost certainly a distribution of electric charge, such that the metal atoms may be regarded as cations embedded

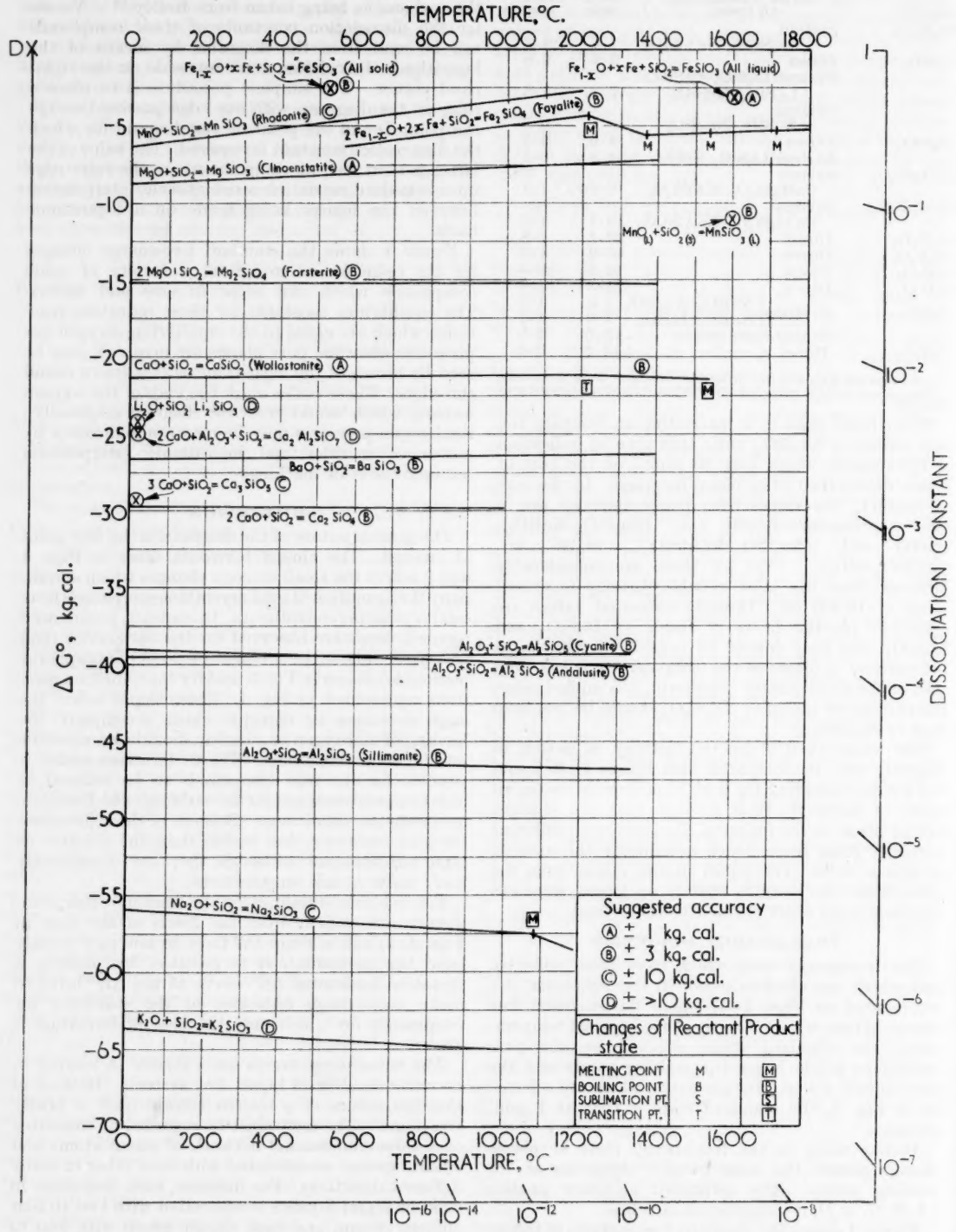


Fig. 1—Free energies of formation of silicates (the curves for the silicates of aluminium have been drawn as explained in the Addendum)

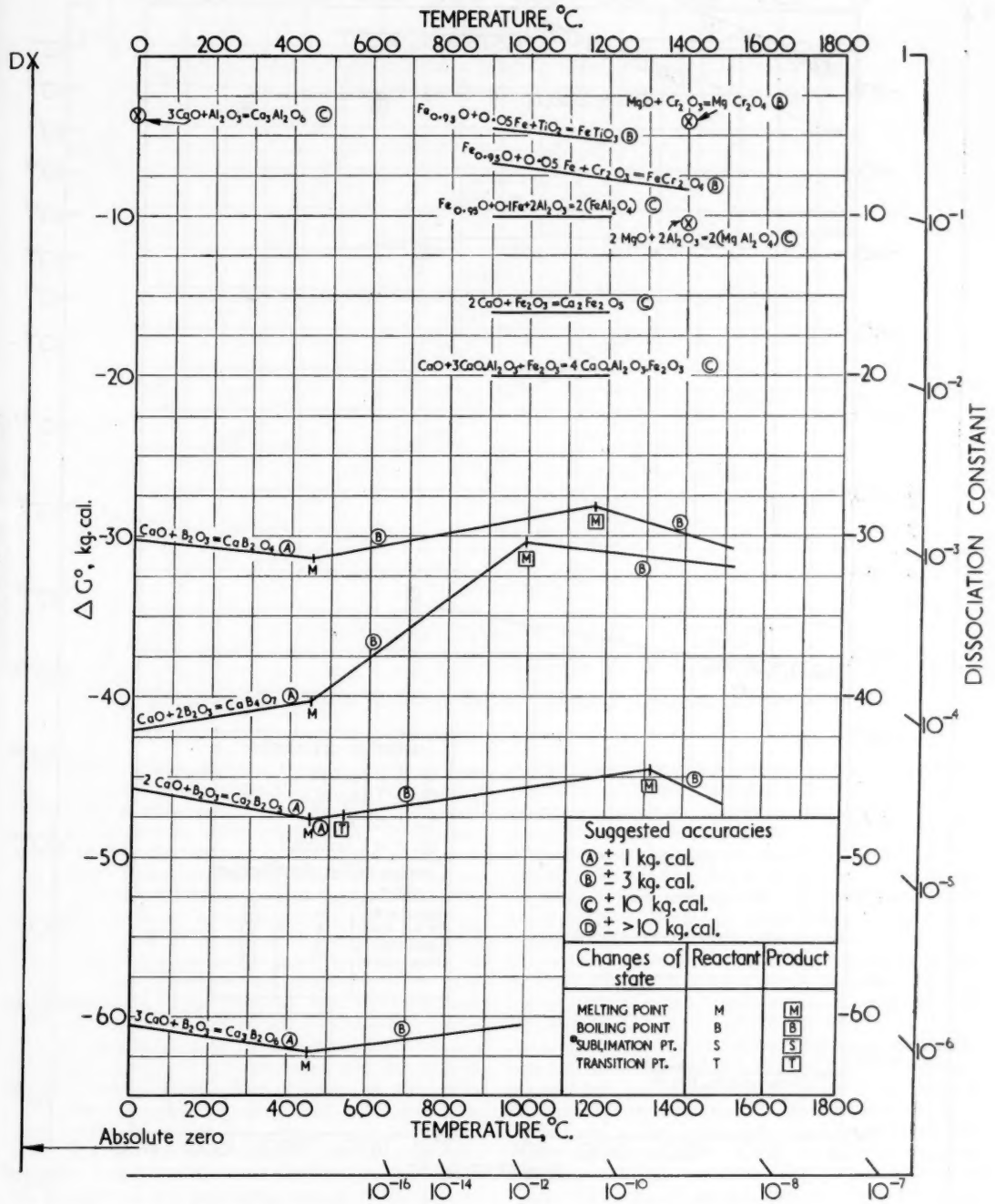


Fig. 2—Free energies of formation of various compounds between oxides

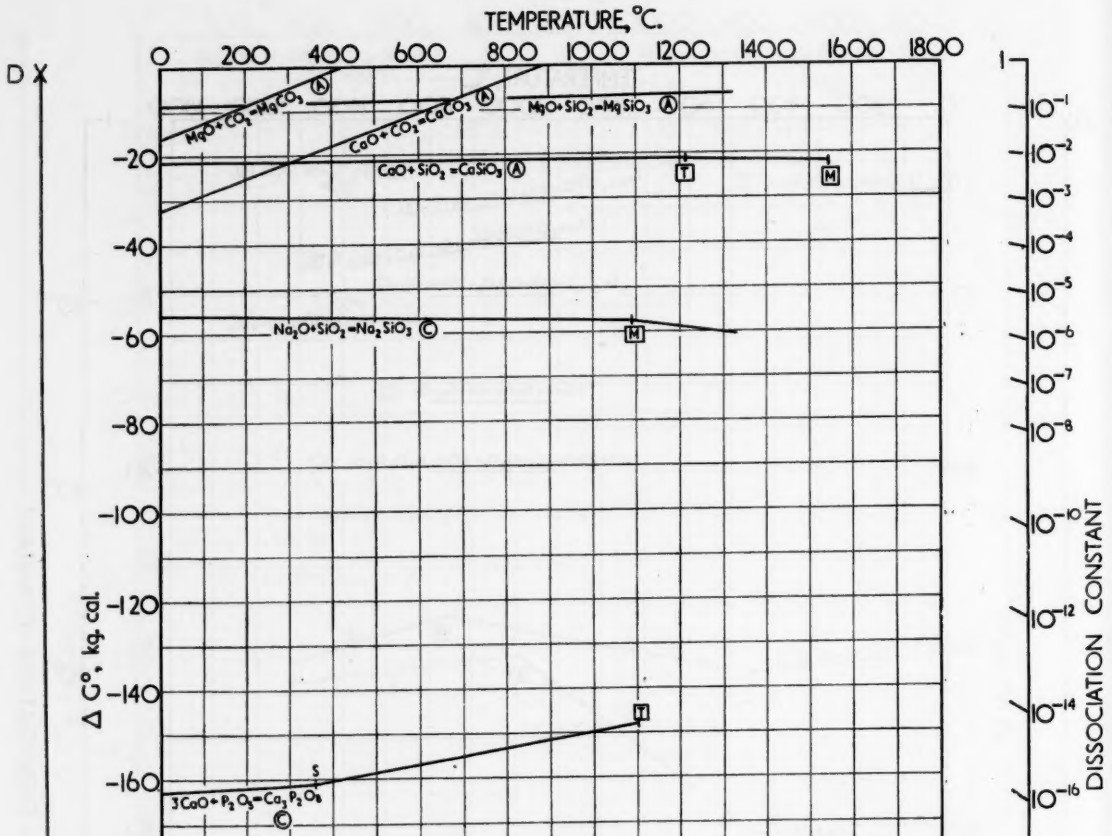

TEMPERATURE, °C.
0 200 400 600 800 1000 1200 1400 1600 1800
D X
Δ G°, kg. cal.
-20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280
MgO+CO2=MgCO3 (A)
CaO+CO2=CaCO3 (A)
MgO+SiO2=MgSiO3 (A)
CaO+SiO2=CaSiO3 (A)
Na2O+SiO2=Na2SiO3 (C)
3CaO+P2O5=Ca3P2O8 (C)
3 Na2O+P2O5=2 Na3PO4 (D)
T
M
S
Suggested accuracies
(A) ± 1 kg. cal.
(B) ± 3 kg. cal.
(C) ± 10 kg. cal.
(D) ± >10 kg. cal.
Changes of state | Reactant | Product
MELTING POINT M M
BOILING POINT B B
SUBLIMATION PT. S S
TRANSITION PT. T T
1 10-1 10-2 10-3 10-4 10-5 10-6 10-7 10-8 10-10 10-12 10-14 10-16 10-18 10-20 10-22 10-24 10-26 10-28
DISSOCIATION CONSTANT
10-50 10-42 10-38 10-34 10-30

Fig. 3—Free energies of formation of some phosphates, silicates, and carbonates

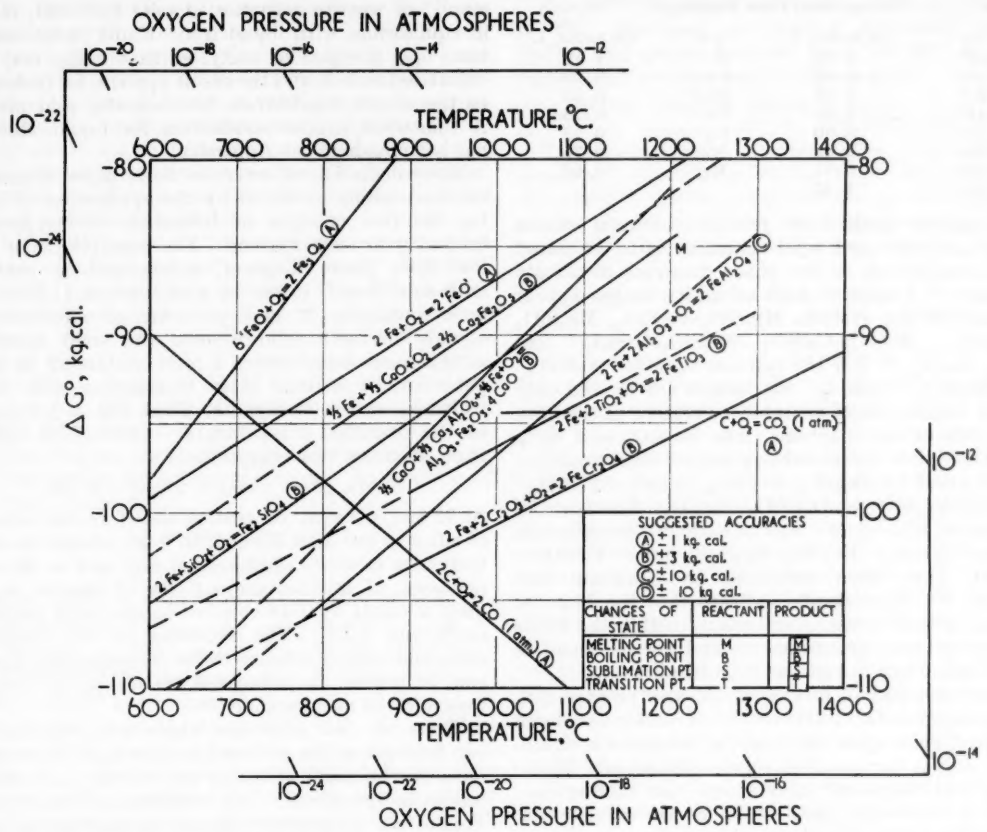


Fig. 4—Free-energy changes accompanying the reduction of various compounds of iron

in an anionic silicate matrix. From the thermodynamic standpoint of slag–metal equilibria this charge distribution is of no significance, though it may well be of importance in other connections. Such a slag cannot be described in terms of *molecules* of silica or iron oxide. These entities may exist only in the gas phase, and they have no physical significance, either in silicate melts or even in pure silica or wüstite. One cannot speak of fayalite dissociating in the liquid to give so much silica and so much ferrous oxide, for neither of these *substances* can be considered to exist in silicate melts. The properties of such a melt may, however, be described in terms of silica and wüstite, with no suggestion that these substances have any identifiable existence in it, provided that this is done on an activity basis. The activity of the silica $a_{(SiO_2)}$, for example, in such a slag is defined precisely by the expression, $\log_{10} a_{(SiO_2)} = -\Delta G/_{2{\cdot}303\,RT}$, where R is the gas constant, T is the absolute temperature, and ΔG is the work involved in the reversible transfer of 1 g. molecular weight of silica from pure silica to a melt of the particular composition concerned at constant pressure and temperature. ΔG° is also equal to the chemical potential ($\Delta\mu$) of the dissolved silica in the melt relative to pure silica.

The application of the free-energy data given in this paper to problems involving liquid slags would be more general were it possible to assume that the various compounds dissociated, and that the product of dissociation behaved in an ideal manner in that liquid. This is not normal for silicate melts, as can be seen by reference to the parts of the activity concentration diagrams, which have already been calculated and reported in the literature.[90, 93] It is interesting to see, however, with what types of slag mixture ideality has been found to exist, so that the conditions under which it can be expected may be recognized.

In the liquid state it is certain, from slag–metal equilibrium measurements, that mixtures of manganese and iron oxides behave ideally,[59, 60] and there is fairly strong evidence that liquid mixtures of oxides of iron and nickel, iron and cobalt, and nickel and cobalt are also ideal.[42, 43] As can be seen from the following data these oxides have cations of similar charge and roughly similar radius. They also show complete or wide ranges of inter-solubility in the solid state. Such properties may be taken as a pointer to ideal behaviour in liquid mixtures. Ideality may, therefore, be expected for the oxides FeO–MgO, NiO–MgO, MgO–MnO, CaO–MnO, Al_2O_3–Cr_2O_3.[37, 44]

Values taken from Pauling[86]

Ion	Ion Radius, Å.	Ion	Ion Radius, Å.
Li^+	0·60	Sr^{++}	1·13
Na^+	0·95	Ca^{++}	0·99
K^+	1·33	Mn^{++}	0·80
Al^{3+}	0·50	Fe^{++}	0·75
Fe^{3+}	0·60	Co^{++}	0·72
Mn^{3+}	0·62	Ni^{++}	0·70
Cr^{3+}	0·64	Mg^{++}	0·65
Ba^{++}	1·35		

A similar qualitative relation between cation charge and size and solid solubility is to be found from examination of the phase diagrams of silicate mixtures.[37] Complete solid solubility ranges appear to exist for the systems Mg_2SiO_4–Fe_2SiO_4, Mn_2SiO_4–Fe_2SiO_4, $MnSiO_3$–$CaSiO_3$, $CaSiO_3$–$SrSiO_3$, and $SrCO_3$–$BaCO_3$.[25] For the systems $MgSiO_3$–"$FeSiO_3$," and $MnSiO_3$–"$FeSiO_3$," the ranges are limited only by the breakdown of unstable "$FeSiO_3$," at the iron-rich ends of the diagrams, into Fe_2SiO_4 and SiO_2. Restricted, but considerable, ranges of solid solubility are reported for Ca_2SiO_4–Fe_2SiO_4, $CaSiO_3$–"$FeSiO_3$," Ca_2SiO_4–Mg_2SiO_4, and $CaSiO_3$–$MgSiO_3$. The heats of solution in hydrofluoric acid of various solid solutions in the systems Fe_2SiO_4–Mg_2SiO_4 and "$FeSiO_3$"–$MgSiO_3$ have been measured by Torgeson and Sahama.[123] Their results indicate that the heats of mixing in both systems are mainly within the limits of error of their measurements and are too small to cause significant deviations from ideality.

Ideal entropies of mixing would also be expected. In the liquid state, ideal entropies of mixing have been observed even when the heats of mixing are significant—this is the so-called regular behaviour. Hildebrand and Salström[38] have shown that molten mixtures of silver and alkali bromides are regular solutions; the same has been shown for mixtures of calcium and alkali carbonates by Flood, Förland, and Roald.[27] The heats of mixing in these cases are significant, for, at infinite dilution of calcium carbonate, these have been found to be — 11,500 cal./mole of $CaCO_3$ in potassium carbonate and — 5500 and — 2400 in sodium and lithium carbonates respectively. These heats are considerably greater than those exhibited by the mixtures of silver and alkali bromides, probably because of the differences between the valencies of the calcium and alkali cations. It seems reasonable, therefore, to assume that liquid, and probably solid, solutions of similar silicates of metals of similar ionic charge and size will behave ideally with respect to the *two silicates*. It is not expected, however, that such mixtures should behave ideally with respect to the *constituent oxides*.

The data from the free-energy diagrams given in this paper may be used to eke out data from other sources, and so provide useful thermodynamic information about silicate melts.[93] In the case of molten fayalite, for example, Fig. 1 shows that :

$$\Delta G^\circ_{1600^\circ C.} = -5800 \text{ cal.} = -RT \log (\text{Dissociation constant})$$

From this it follows that :

$$a^2_{(Fe_{1-x}O)} \times a_{(SiO_2)} \times a^{2x}_{[Fe]} = 0{\cdot}21$$

A value of 0·66 for the activity of wüstite, $a_{(Fe_{1-x}O)}$, in a slag corresponding to liquid fayalite, can be derived from the measurements by Taylor and Chipman[117] of wüstite activities in CaO–FeO–SiO_2 melts in equilibrium with liquid iron. Under these conditions $a_{(Fe)}$ is equal to unity, so that $a_{(SiO_2)}$ may be calculated as 0·5, and the result applied, for instance, to the silicon equilibrium between slag and metal. A somewhat similar calculation for liquid $MnSiO_3$ has been made in the Appendix.

The calculation of activities from phase diagrams can be usefully extended by the application of data for the free energies of formation of compounds occurring in such systems. For example, from the FeO–SiO_2 phase diagram, determined in contact with solid iron,[37] it can be seen that, at 1175° C., a melt containing 73 mol. per cent. of wüstite is in equilibrium with solid wüstite and solid fayalite; at this same temperature a melt containing 58 mol. per cent. of wüstite is in equilibrium with solid tridymite and solid fayalite. From Fig. 1 $\Delta G^\circ_{1175^\circ C.}$, for the formation of fayalite, is — 4200 cal. It follows that, at these two compositions :

$$a^2_{(Fe_{1-x}O)} \times a_{(SiO_2)} \times a^{2x}_{[Fe]} = 0{\cdot}23$$

At 73 mol. per cent. of wüstite, therefore, the activity of silica in the melt is equal to 0·23 relative to solid tridymite (activity coefficient 0·85), and at 58 mol. per cent. of wüstite, the activity of wüstite in the melt is equal to 0·48 relative to the solid (activity coefficient 0·83). The activities of the dissolved silica and wüstite relative to the corresponding liquids can, of course, be calculated *via* the latent heat of fusion in the usual manner.[13]

There are few instances where such calculations can be made at the present time, owing to the lack of data on the heats of fusion and on the activities of oxides in slag melts. The usefulness of this type of application is, however, bound to increase as more data become available.

Acknowledgment

The authors are indebted to Mrs. U. Ende for general assistance and, in particular, for graphing much of the original data and evaluating heat contents and entropies from them.

APPENDIX

Many of the free-energy equations given below are based on those proposed in Part I. A number of equations from Part I have been revised in the light of subsequent experience, and in such cases new equations are quoted for the formation of the oxides concerned, as well as for the compounds between them.

Except in cases where equilibrium data are available, calculations have been made on the basis of the heat theorem. Unless otherwise stated the heat-capacity data, the entropies at 298° K., and the heat and entropy changes accompanying changes of state have been taken from the Tables at the end of the Appendix.

As in Part I, an attempt has been made to estimate the accuracy of the free-energy equations, each of which has been graded into one of the following classes :

A : ± 1 kg.cal.	C : ± 10 kg.cal.
B : ± 3 ,,	D : ± >10 ,,

The limits proposed for each class are the limits within which the true values of ΔG° almost certainly lie (probability, say, 95%). The limits take into account the spread of the data selected as most reliable, the extent to which they may be extrapolated, and the opinion of the authors concerning the likely accuracies of the techniques employed and the reliability of the various investigators. The authors, therefore, wish to stress that the gradings have no precise statistical significance.

The crystalline states of the substances represented in the equations are indicated in cases where the accuracy justifies their inclusion. In the case of silica, however, the heat and entropy changes accompanying the transitions from quartz to tridymite (120 ± 50 cal. at 1140° K.), and tridymite to cristobalite (50 ± 50 cal. at 1743° K.),[77] are, in all cases, smaller than the limits of accuracy assigned.*

The order of the substances is alphabetical. All the iron compounds are brought together under iron; the remainder are introduced under the heading of the more basic metal.

DATA USED

Aluminium

Silicate ($Al_2O_3 + SiO_2 = Al_2SiO_5$). Accuracy *B*

Andalusite	$\Delta G^\circ_{298\text{–}1600^\circ\text{K.}} = -39{,}050 - 5{\cdot}4\,T$
Cyanite	$\Delta G^\circ_{298\text{–}1600^\circ\text{K.}} = -39{,}600 + 0{\cdot}9\,T$
Sillimanite	$\Delta G^\circ_{298\text{–}1600^\circ\text{K.}} = -45{,}950 - 2{\cdot}5\,T$

Neumann[85] has measured the heats of solution of all three forms of Al_2SiO_5 in 40% HF. Klever[58] has measured the heats of solution of quartz and of a series of hydrated aluminas in 40% HF. He has plotted $\Delta H_{soln.}$ against the percentage of water in the aluminas, and has extrapolated to obtain the heat of solution of pure alumina, as this cannot be determined directly. The following heats of formation were derived from these measurements:

$\Delta H^\circ_{298^\circ\text{K.}}$ (Andalusite)	$= -39{,}350$
$\Delta H^\circ_{298^\circ\text{K.}}$ (Cyanite)	$= -39{,}750$
$\Delta H^\circ_{298^\circ\text{K.}}$ (Sillimanite)	$= -45{,}950$

These values were combined with the heat-capacity data given in the Tables to obtain values of ΔG°, which can be represented by the linear equations proposed above within the likely error limits of all the data employed.

BARIUM

Silicate ($BaO + SiO_2 = BaSiO_3$). Accuracy *B*

$$\Delta G^\circ_{298\text{–}1600^\circ\text{K.}} = -26{,}800 + 0{\cdot}1\,T$$

Jander[41] has measured the equilibrium pressure of CO_2 developed on heating intimately mixed $BaCO_3$ and quartz between *circa* 700–900° C. His results may be expressed by the equation:

$$BaCO_3 + SiO_2 = BaSiO_3 + CO_2, \quad \Delta G^\circ = -35{,}100 + 36{\cdot}4\,T$$

Finkelstein[26] has measured the CO_2 pressure developed on heating $BaCO_3$ alone between *circa* 900–1300° C. He has found that the reaction proceeds in two steps, owing to the formation of a basic carbonate. His results may be represented by the equations:

$$2BaCO_3 = BaO.BaCO_3 + CO_2, \quad \Delta G^\circ = -66{,}000 + 40{\cdot}6\,T$$

$$BaO.BaCO_3 = 2BaO + CO_2, \quad \Delta G^\circ = -59{,}800 + 34{\cdot}6\,T$$

By combining Finkelstein's and Jander's results the free-energy equation for the formation of the silicate from barium oxide and silica can be obtained.

The temperature-dependent term cannot be considered to be very accurate, because of the scatter of the two sets of results and because it was obtained by compounding three equations. There are insufficient thermal data to permit an independent check to be made on this term by means of the heat theorem. By analogy with the reaction with $CaO + SiO_2 = CaSiO_3$, for which the temperature-dependent term is accurately known, it appears that its value must be very small. The free-energy line for $BaSiO_3$ in Fig. 1 has, therefore, been drawn by taking the value of ΔG° at 1200° K. (— 26,400) from these experimental results and by drawing a line through this, parallel to that for $CaSiO_3$.

The work of Jander has been extended to other barium silicates by Grube and Trucksess,[36] but their results are not considered to be sufficiently reliable for thermodynamic calculations.

CALCIUM

Aluminates ($3CaO + Al_2O_3 = Ca_3Al_2O_6$). Accuracy *C*

$$\Delta G^\circ_{298^\circ\text{K.}} = -3700$$

Thorvaldson, Brown, and Peaker[119] have measured the heat of solution of $Ca_3Al_2O_6$ in $HCl.20H_2O$, and the heat of dilution of the resulting solution to $HCl.200H_2O$. They have also measured the corresponding heat of solution of CaO.[120]

They have calculated the heat of solution of Al_2O_3 from the heat of solution of aluminium measured by Richards, Rowe, and Burgess,[91] from Roth and Müller's[98] value of the heat of the reaction $Al + \frac{3}{2}O_2 = \frac{1}{2}Al_2O_3$ ($\Delta H^\circ_{298^\circ\text{K.}} = -190{,}000$ cal.), and from Lewis's value[67] for the heat of formation of water. The value for the heat of formation of alumina was corrected to the value — 199,500 cal., owing to the more recent determination by Snyder and Seltz.[112] These results combine to give $\Delta H^\circ_{298^\circ\text{K.}} = -2700$ cal. for the reaction $3CaO + Al_2O_3 = Ca_3Al_2O_6$.

Free-energy equations cannot be recommended as $S^\circ_{298^\circ\text{K.}}$ is not known for $Ca_3Al_2O_6$; the value for $\Delta G^\circ_{298^\circ\text{K.}}$ was calculated on the assumption that ΔS°_{298} is approximately the same as for $Ca_3B_2O_6$, *i.e.*, + 4 cal./degree.

($5CaO + 3Al_2O_3 = 5CaO.3Al_2O_3$), Accuracy *D*

$$\Delta G^\circ_{298^\circ\text{K.}} = 0$$

*Acceptance of the values for the heats of transformation of silica, which are those recommended by Mosesman and Pitzer,[77] makes it necessary to abandon the heat of formation of quartz recommended in Part I, on the basis of the work of Roth, Becker, and Troitzsch.[94] When Roth and Becker's measured heat of formation of cristobalite (−205,600) is combined with Mosesman and Pitzer's heat of transformation of cristobalite to quartz (-354 ± 100 at 298° K.), the heat of formation of quartz becomes −205,800. This compares with −208,300 which was previously recommended on the basis of Roth and Troitzsch's value of −2700 for the heat of transformation of cristobalite to quartz at 298° K. It is difficult to choose between these values for the heats of transformation; as −2700 seems rather large, it is considered safer to accept the lower value until substantiating measurements become available.

Roth and Wolf[101] have measured the heat of solution of $5CaO.3Al_2O_3$ and of lime in 6·65*N* HCl at 20° C. They have calculated the heat of solution of aluminium for the same conditions, by applying corrections to the measurements by Richards, Rowe, and Burgess[91] referred to under $Ca_3Al_2O_6$. From these results, and the heat of formation of alumina and of water also referred to under $Ca_3Al_2O_6$, the heat of formation at 20° C. of $5CaO.3Al_2O_3$ from its oxides may be calculated as — 400 cal. Because of the indirect nature of the calculation and the large and rather doubtful correction which had to be applied to the results of Richards, Rowe, and Burgess, this figure can hardly be classed better than accuracy *D*. A tentative value of zero has therefore been assigned to $\Delta G^\circ_{298^\circ K.}$.

Borates ($3CaO + B_2O_3 = Ca_3B_2O_6$)

$\Delta G^\circ_{298-723^\circ K.} = -59{,}450 - 4{\cdot}03\,T.$ Accuracy *A*
$\Delta G^\circ_{723-1200^\circ K.} = -64{,}720 + 3{\cdot}26\,T.$ „ *B*

($2CaO + B_2O_3 = Ca_2B_2O_5$)

$\Delta G^\circ_{298-723^\circ K.} = -45{,}900 - 2{\cdot}42\,T.$ Accuracy *A*
$\Delta G^\circ_{723-804^\circ K.} = -51{,}170 + 4{\cdot}87\,T.$ „ *A*
$\Delta G^\circ_{804-1585^\circ K.} = -50{,}070 + 3{\cdot}50\,T.$ „ *B*
$\Delta G^\circ_{1585-1700^\circ K.} = -25{,}980 - 11{\cdot}70\,T.$ „ *B*

($CaO + B_2O_3 = CaB_2O_4$)

$\Delta G^\circ_{298-723^\circ K.} = -29{,}400 - 2{\cdot}73\,T.$ Accuracy *A*
$\Delta G^\circ_{723-1435^\circ K.} = -34{,}670 + 4{\cdot}56\,T.$ „ *B*
$\Delta G^\circ_{1435-1700^\circ K.} = -17{,}000 - 7{\cdot}75\,T.$ „ *B*

($CaO + 2B_2O_3 = CaB_4O_7$)

$\Delta G^\circ_{298-723^\circ K.} = -43{,}100 + 3{\cdot}90\,T.$ Accuracy *A*
$\Delta G^\circ_{723-1260^\circ K.} = -53{,}640 + 18{\cdot}50\,T.$ „ *B*
$\Delta G^\circ_{1260-1700^\circ K.} = -26{,}580 - 3{\cdot}00\,T.$ „ *B*

Torgeson and Shomate[124] have made most careful measurements of the heats of solution of all these calcium borates, and of the appropriate mixtures of CaO and B_2O_3 in normal HCl at 25° C. Their values for ΔH°_{298} were used here. It is interesting to compare these with the values obtained, much earlier, by Griveau.[33]

Heats of Formation from Oxides

	Torgeson and Shomate	Griveau
$CaO.B_2O_3$	— 29,420	(— 30,900)
$CaO.2B_2O_3$	— 42,930	(— 39,800)
$2CaO.B_2O_3$	— 45,760	(— 48,500)
$3CaO.B_2O_3$	— 60,000	(— 62,000)

Phosphate ($3CaO + P_2O_5 = Ca_3P_2O_8$). Accuracy *C*

$\Delta G^\circ_{298-631^\circ K.} = -164{,}000 + 4{\cdot}22\,T$
$\Delta G^\circ_{631-1373^\circ K.} = -172{,}800 + 18{\cdot}16\,T$

Matignon and Séon[75] have measured the heats of solution in *N*/2 HCl of $Ca_3P_2O_8$, CaO, and H_3PO_4, and the heat of mixing of the resultant solutions of the last two substances. Frandsen[29] has determined the heat of solution of P_2O_5 in water to give H_3PO_4 in very dilute solution. The heat of solution cannot be measured directly, since both HPO_3 and H_3PO_4 are formed when the P_2O_5 is dissolved. Because of this, and because the heat of mixing H_3PO_4 and HCl solutions is not known, and has, therefore, been taken as zero, calculations from these results are somewhat uncertain. The heat equations are :

$$Ca_3P_2O_8 + 6HCl\ (N/2) = 3CaCl_2 + 2H_3PO_4, \quad \Delta H = -28{,}450$$

$$3CaO + 6HCl\ (N/2) = 3CaCl_2 + 3H_2O, \quad \Delta H = -138{,}300$$

$$2H_3PO_{4(\text{dil. in } N/2\ HCl)} + 3CaCl_{2(\text{dil. in } N/2\ HCl)} = 2H_3PO_4 + 3CaCl_2, \quad \Delta H = +240$$

$$P_2O_5 + \text{aq.} = 2H_3PO_{4(\text{aq.})}, \quad \Delta H = -54{,}400$$

From these equations can be calculated :

$$3CaO + P_2O_5 = Ca_3P_2O_8, \Delta H = -164{,}000$$

Silicates (Wollastonite) ($CaO + SiO_2 = CaSiO_3$)

$\Delta G^\circ_{298-1483^\circ K.} = -21{,}300 + 0{\cdot}12\,T.$ Accuracy *A*
$\Delta G^\circ_{1483-1813^\circ K.} = -19{,}900 - 0{\cdot}82\,T.$ „ *B*

Torgeson and Sahama[123] have measured the heat of solution of CaO, SiO_2 (quartz), and $CaSiO_3$ (wollastonite) in 20% HF at 73·7° C. The scatter of their individual measurements is very small, and their figure of — 21,250 for $\Delta H^\circ_{298^\circ K.}$ was accepted for this reaction. Since allowance was not made for the heat of mixing of the products of solution of CaO and SiO_2 in HF and the allowance made for the impurities in the β $CaSiO_3$ was an approximation, the safe error limit is considered to be nearer $\pm$ 500 cal. than the 130 cal. claimed by Torgeson and Sahama.

Noteworthy determinations of this ΔH have also been made by Roth and Chall[97] ($\Delta H = -19{,}660$), Wagner[129] ($\Delta H = -21{,}460$), and Roth and Troitzsch[99] ($\Delta H = -21{,}750$).

The mean of these determinations agrees with Torgeson and Sahama's value.

($2CaO + SiO_2 = Ca_2SiO_{4(\beta)}$). Accuracy *B*
$\Delta H^\circ_{298^\circ K.} = -29{,}800$

Johannsen and Thorvaldson[45] have measured the heat of reaction of $Ca_2SiO_{4(\beta)}$ with $HCl.20H_2O$ to give calcium chloride in solution and gelatinous silica. They have also measured the heat of diluting the solution produced to that which would be obtained if $HCl.200H_2O$ had been used as solvent. Using the values of Thorvaldsen, Brown, and Peaker[120] for the heat of solution of CaO in $HCl.200H_2O$, it is possible to calculate :

$$2CaO + SiO_{2(\text{gel. } x\%H_2O)} = Ca_2SiO_{4(\beta)}, \quad \Delta H^\circ_{298^\circ K.} = -33{,}240$$

It is, unfortunately, difficult to estimate with any reliability the heat of the reaction :

$$SiO_{2(\text{gel. } x\%H_2O)} \rightarrow SiO_{2(\text{quartz})} + xH_2O$$

Roth and Chall[97] have measured the heats of solution in 20% hydrofluoric acid of : (*a*) gelatinous silica, obtained by treating $CaSiO_{3(\beta)}$ with HCl, and (*b*) quartz. They give the heat of the reaction as — 3425 cal., but the figure can be approximate only, since gelatinous silica is an indeterminate substance. It was used here to calculate $\Delta H^\circ_{298^\circ K.} = -29{,}800$ for the reaction :

$$2CaO + SiO_{2(\text{quartz})} = Ca_2SiO_{4(\beta)}$$

As there is no value for $S^\circ_{298^\circ K.}$ for Ca_2SiO_4, a free-energy equation cannot be given. The line in Fig. 1 is drawn on the assumption that ΔS° is negligible, as for Mg_2SiO_4. The data in Table II show that $\Delta G^\circ_{1200^\circ K.}$ is not significantly different from $\Delta G^\circ_{298^\circ K.}$

Pidgeon and King,[87] using an entrainment technique, have measured the magnesium pressure associated with the equilibrium :

$$2MgO + 2CaO + Si(Fe) = Ca_2SiO_4 + 2Mg_{(gas)} + Fe$$

The results lead to values for the free energy of formation of Ca_2SiO_4 far more negative than are recommended here. The solid products of the reaction were not identified, and the results are not considered as reliable as the heat of solution data.

$(3CaO + SiO_2 = Ca_3SiO_5)$. Accuracy *C*

$$\Delta H^\circ_{298^\circ K.} = -29{,}350$$

The results of Johannsen and Thorvaldson[45] were used. The figure calculated for $\Delta H^\circ_{298^\circ K.}$ suffers from the same disadvantage as that for Ca_2SiO_4, owing to the indefinite nature of gelatinous silica.

In the absence of entropy data for Ca_3SiO_5, a free-energy equation cannot be recommended. $\Delta G^\circ_{298^\circ K.}$, given in Fig. 1, is based on the assumption that $\Delta S^\circ_{298^\circ K.}$ is trivial. Since Ca_3SiO_5 appears to be stable with respect to CaO and Ca_2SiO_4 between 1100° and 1900° C., the ΔG° curve for Ca_3SiO_5 should lie below that for Ca_2SiO_4 in that range. Shadduck[105] has applied the existing specific heat data on lime and these two silicates to this matter, but it is questionable whether the accuracy of the data is sufficient to warrant this.

Gehlenite $(2CaO + Al_2O_3 + SiO_2 = 2CaO.Al_2O_3.SiO_2)$. Accuracy *D*

$$\Delta H^\circ_{298^\circ K.} = -24{,}900$$

Eitel and Richter[22] have quoted the heat of this reaction as $\Delta H^\circ_{298^\circ K.} = -24{,}900$ cal. This figure is based on the heat of solution of $2CaO.Al_2O_3.SiO_2$, lime and silica in an HNO_3/HF mixture, and a *calculation* of the heat of solution of Al_2O_3 under the same conditions. As the heat of solution of Al_2O_3 is unverifiable, the calculated heat of formation of gehlenite is rather doubtful.

In the absence of entropy data for gehlenite no free-energy equation can be recommended; the value of $\Delta G^\circ_{298^\circ K.}$, shown in Fig. 2, is based on the assumption that $\Delta S^\circ_{298^\circ K.}$ is trivial.

IRON

Aluminate $(2Fe + O_2 + 2Al_2O_3 = 2FeAl_2O_4)$. Accuracy *C*

$$\Delta G^\circ_{1100\text{–}1400^\circ K.} = -150{,}000 + 41{\cdot}80\ T$$

This equilibrium has been studied by Cirilli[16] between 900° and 1100° C. by means of CO/CO_2 gas mixtures, but it has been approached from the CO-rich side only. The temperature-dependent term in the equation seems suspiciously large. In view of the small temperature range investigated, it is not possible to attach any significance to the separate ΔH° and ΔS° terms of the equation.

$(0{\cdot}10Fe + 2Fe_{0{\cdot}95}O + 2Al_2O_3 = 2FeAl_2O_4)$. Accuracy *C*

$$\Delta G^\circ_{1100\text{–}1400^\circ K.} = (-24{,}300 + 11{\cdot}1\ T) = \textit{circa} -10{,}000$$

The formation of iron aluminate from wüstite requires the addition of free iron, owing to the non-stoichiometry of wüstite. The equation was calculated from that quoted for the reduction of $2FeAl_2O_4$, by adding the following equation, which is referred to in more detail in the section relating to wüstite :

$$2Fe_{0{\cdot}95}O = 1{\cdot}9Fe + O_2,$$
$$\Delta G^\circ_{1173\text{–}1644^\circ K.} = +125{,}700 - 30{\cdot}69\ T.$$

It is considered that the trend of ΔG° with temperature for the formation of the aluminate may be in error, as the entropy term seems suspiciously large. It is probably safest to accept 10 kg. cal. as the appropriate value of ΔG° in this temperature range.

The equilibrium between nickel, alumina and nickel aluminate, and CO/CO_2 gas mixtures has been studied by Fricke and Weitbrecht[30] from 800 to 1000° C. They found that the "equilibrium" CO/CO_2 ratio was dependent on whether equilibrium was approached with reducing or oxidizing gas mixtures, and, if oxidizing, on the duration of the experiment. They concluded that, under reducing conditions, the solids participating in the equilibrium were very finely divided nickel and alumina, and that the free energy of formation of nickel aluminate, determined for these conditions, might be more negative than for the bulk phase by as much as 5 kg.cal./mole. No such trouble was observed for the corresponding Ni–NiO equilibrium, so that the effect appeared to be associated with the presence of two finely divided solid reaction products, which prevented each other from sintering into crystals large enough to be representative of the bulk phases. The results throw doubt on the validity of free energies of formation of compounds between oxides calculated from oxidation/reduction equilibria, especially when the equilibria have been approached only by reduction of the solid, and the particle size of the products has not been checked.

Brownmillerite $\frac{2}{3}(CaO + Ca_3Al_2O_6 + 2Fe + \frac{3}{2}O_2 = Al_2O_3.Fe_2O_3.4CaO)$. Accuracy *C*

$$\Delta G^\circ_{1100\text{–}1400^\circ K.} = -155{,}000 + 49{\cdot}7\ T$$

The oxidation reduction equilibrium of brownmillerite with CO/CO_2 gas mixtures has been studied by Malquori and Cirilli[69] from 900 to 1100° C.; the equilibrium has, however, been approached from the CO-rich side only, so that the value of their results may be open to the objection referred to under ferrous aluminate (*see* this page). The results lead to the equation given here when compounded with the CO–CO_2 equation cited in Part I.[94] Although the ΔG° values may be reasonably accurate over the short temperature range investigated, the individual terms in the equation cannot be taken with certainty as approximating ΔG° and ΔS°.

$(CaO + 3CaO.Al_2O_3 + Fe_2O_3 = 4CaO.Al_2O_3.Fe_2O_3)$. Accuracy *C*

$$\Delta G^\circ_{1100\text{–}1400^\circ K.} = -20{,}000$$

When the equation for the reduction of brownmillerite is compounded with equations (*a*) and (*b*) cited under dicalcium ferrite (page 225), the above value of ΔG° is obtained. A suspiciously large value of $\Delta S^\circ = -12$ cal./degree is obtained in this way. As with dicalcium ferrite, it is not likely to be significant, owing to the small temperature range of Cirilli's results and the errors which may arise from compound-

Table I—THERMAL DATA FOR OXIDES

Oxide	$H_{298}-H_0$	S_{298}	T = 500° K.		T = 1000° K.		T = 1200° K.		T = 1500° K.	
			H_T-H_{298}	S_T-S_{298}	H_T-H_{298}	S_T-S_{298}	H_T-H_{298}	S_T-S_{298}	H_T-H_{298}	S_T-S_{298}
Al_2O_3—α	2440 ± 20	12·5 ± 0·15	4600 ± 50	11·67 ± 0·12	18890 ± 190	31·32 ± 0·31	24740 ± 250	36·64 ± 0·37	33980 ± 340	43·51 ± 0·44
B_2O_3	2257 ± 20	13·04 ± 0·1	3670 ± 40	9·39 ± 0·09	23900 ± 240	35·21 ± 0·35	29950 ± 300	40·82 ± 0·41	39200 ± 390	47·75 ± 0·48
CaO	1688 ± 30	9·5 ± 0·2	2310 ± 50	5·73 ± 0·11	8990 ± 180	14·81 ± 0·29	12040 ± 240	17·6 ± 0·35		
Cr_2O_3	3710 ± 50	19·4 ± 0·3	5340 ± 50	13·73 ± 0·14	20040 ± 200	34·01 ± 0·34	26227 ± 260	39·65 ± 0·40	35590 ± 360	46·61 ± 0·47
Fe_2O_3	3800 ± 80	21·5 ± 0·5	5680 ± 110	14·19 ± 0·23	23500 ± 470	39·13 ± 0·78				
"FeO" (wüstite)										
MgO	1300 ± 30	6·55 ± 0·15	2000 ± 40	5·12 ± 0·10	7680 ± 150	13·09 ± 0·26	10020 ± 200	15·30 ± 0·31	13760 ± 280	17·85 ± 0·36
MnO	2000 ± 20	14·4 ± 0·6	2280 ± 20	5·82 ± 0·06	8430 ± 80	14·3 ± 0·14	11100 ± 110	15·86 ± 0·16	15210 ± 150	19·79 ± 0·20
Na_2O		17·5 ± 1·0 (estimated)	3650 ± 190	9·38 ± 0·47	13620 ± 680	23·04 ± 1·15				
P_4O_{10}		67·0 ± 4·0	11880 ± 240	30·0 ± 0·6	66750 ± 2000	109·25 ± 3·28	81200 ± 2440	121·1 ± 3·63		
SiO_2	1660 ± 20 (quartz)	10·01 ± 0·1 (quartz)	2560 ± 5	6·48 ± 0·1	10920 ± 110	17·93 ± 0·1	14380 ± 140	21·08 ± 0·1	19530 ± 200	24·91 ± 0·1
TiO_2	2080 ± 20	12·01 ± 0·05	3100 ± 30	7·93 ± 0·08	11650 ± 120	19·72 ± 0·20	15200 ± 150	22·96 ± 0·23	20660 ± 200	27·02 ± 0·27

ing three equations. A temperature-dependent term is, therefore, not given in the recommended ΔG° equation.

Richter[95] and Lerch and Brownmiller[66] have measured the heat of solution of brownmillerite in HF/HNO_3 mixtures, and Thorvaldson, Edwards, and Bailey[121] have measured its heat of solution in HCl, but the auxiliary data required to calculate its heat of formation from its component oxides are not available.

Chromite ($2Fe + O_2 + 2Cr_2O_3 = 2FeCr_2O_4$).

Accuracy *B*

$$\Delta G^\circ_{1173\text{–}1700^\circ\text{K.}} = -131{,}600 + 24{\cdot}2\,T$$

Boericke and Bangert[3] have measured the equilibrium between H_2/H_2O gas mixtures and the system Fe–Cr_2O_3–$FeCr_2O_4$ between 1270 and 1410° C. Their results are probably affected by thermal segregation in the gases, caused by the slow rate of flow in their apparatus. Their results were, therefore, plotted on a $\Delta G^\circ/T$ plot, and a line was drawn through the lower temperature results, where thermal segregation should be a minimum, with a slope equal to $-\Delta S^\circ_{1600^\circ\text{K.}}$ (+ 24·2 cal./degree) calculated from heat-capacity data. The equation for this line, which is given here, leads to ΔG° values which are 1½ kg.cal. more negative than those obtained by Boericke and Bangert at 1410° C.

Table I—*(contd.)*

Other Thermal Data	Remarks
M.P. 2318° K.[49] ΔH_f 26,000[49]	C_p data[46, 110] satisfactory: estimated accuracy ± 1%. Heat of fusion by Kelley[46] from binary systems such as Al_2O_3–TiO_2, Al_2O_3–Al_4C_3 Low-temperature data from Kelley [46]
M.P. 723° K.[51] ΔH_f 5270[113]	C_p data[51, 113] satisfactory, though there is lack of agreement at 298° K.: estimated accuracy ± 1%. ΔH_f has been estimated from heat content data of Southard.[113] M.P. is that of Kracek and others.[52] Cole and Taylor[18] give 567° K.
M.P. 2845° K.[48]	C_p data[47] are reasonably good up to 1200° K., but are probably too high above this. High- and low-temperature data[46] agree satisfactorily between 298° and 1200° K. Estimated accuracy ± 2%.
M.P. 2550° K.[9]	High- and low-temperature C_p data are from Kelley and others[15] and Anderson[1] respectively. Kelley[15] interprets Anderson's C_p anomaly at 298° K. as a precise transition from α to β Cr_2O_3
Dissociation pressure is 1 atm. at 1723° K.[19, 20]	C_p data[47] above 298° K. are reasonably good to 1100° K., estimated accuracy being ± 2%. Lower temperature data are taken from Kelley.[46] The error limits of ± 0·5 in S_{298}[46] are caused by the large extrapolation below 90° K.
M.P. incongruent 1642° K. ΔH_f 7500/gram atom of oxygen at composition $Fe_{0\cdot95}O$[14]	Millar[74] has measured C_p from 70 to 300° K., and White[130] has measured it from 303 to 1173° K. Since there is doubt as to the precise nature of the materials used, and equilibrium data are available for reactions involving wüstite, the thermal data have not been reported
M.P. approx. 3000° K.[49] ΔH_f 18500	C_p data[46, 47] satisfactory. Low-temperature data are taken from Kelley.[46] Kelley[49] has deduced a value of 18,500 cal. for ΔH_f from binary system MgO–ZrO_2, but it can hardly be considered reliable
M.P. 2058° K.[52] ΔH_f 10,700 (approx.)[14]	C_p data[110] satisfactory above 298° K.: estimated accuracy ± 1%. λ pt. between 80 and 140° K. and large extrapolation below 70° K. account for error limits ± 0·6 in S_{298}.[46] ΔH_f quoted from Chipman, Gero, and Winkler[14] is based on the assumption that ΔS fusion for MnO is the same as for FeO
M.P. 1193° K. B.P. > 1873° K.[11]	There are no low-temperature data. S_{298} has been estimated by Shomate[106] from the corresponding entropies of sodium titanates and rutile. Data above 298° K. have been derived by Naylor[85] from a study of heat contents of sodium silicates and titanates, and are not considered to be more accurate than ± 5%
Sublimation point (1 atm.) 631° K. $\Delta H_{subl.}$ 631° K., 17600 ± 2600[29]	No C_p data below 298° K.: the value given for S_{298} is an estimate.[94] Estimated accuracy of data[47, 93] above 298° K. ± 2%; above 631° K. ± 3%
M.P. 1986° K.[21] ΔH_f 1835 Transition: Quartz to tridymite 1140° K. $\Delta H_{tr.}$ 120 ± 50 Tridymite to cristobalite 1743° K. $\Delta H_{tr.}$ 50 ± 50	Mosesman and Pitzer[77] have collated their own data and those of other workers and have estimated thermodynamic functions over the temperature range 298–2000° K. Estimated accuracies $\Delta H_{298-625°\,K.}$ ± 0·2%, $\Delta H_{625-2000°\,K.}$ ± 1%, $\Delta S_{298-2000°\,K.}$ ± 0·1 cal./degree. Heat of fusion is by Kracek[21] from binary system Cs_2O–SiO_2. Transition α to β quartz which takes place over a wide temperature range is included in calculations
M.P. 2098° K.	Low temperature data of Shomate[106] have been preferred to those of McDonald and Seltz.[71] Shomate's data agree satisfactorily with Naylor's high-temperature data at 298° K. Estimated accuracy ± 1%

Boericke and Bangert found they were unable to obtain reproducible results when equilibrium was approached in the oxidizing direction at temperatures below 1300° C. It is thought that this may be due to a particle-size phenomenon, as described under ferrous aluminate (*see* page 223).

($Fe_{0\cdot95}O + 0\cdot05Fe + Cr_2O_3 = FeCr_2O_4$). Accuracy *B*

$$\Delta G°_{1173-1644°\,K.} = -2950 - 3\cdot23\,T$$

This equation was obtained by compounding the equation for the reduction of chromite to free iron with the equation, quoted under wüstite, for the reduction of ferrous oxide.

Dicalcium Ferrite ($\frac{4}{3}CaO + \frac{4}{3}Fe + O_2 = \frac{2}{3}Ca_2Fe_2O_5$). Accuracy *B*

$$\Delta G°_{1100-1400°\,K.} = -132{,}300 + 34\cdot1\,T$$

This oxidation reduction equilibrium has been studied by Malquori and Cirilli[17,69] with CO/CO_2 gas mixtures. The equilibrium has been approached from the CO-rich side only, so that the results may be open to the objection raised under ferrous aluminate (*see* page 223). The results between 900 and 1050° C. give a linear $\Delta G°/T$ plot which leads to the equation just given when combined with the CO, O_2, CO_2 equation cited in Part I.[94] It is considered that this equation is more reliable than the data for the CO, O_2, CO_2 equilibrium used by Malquori and Cirilli for the calculations in their paper.[69]

Table II—THERMAL DATA FOR SILICATES

Silicate	$H_{298}-H_0$	S_{298}	$T = 500°$ K.			$T = 1000°$ K.			$T = 1200°$ K.		
			H_T-H_{298}	S_T-S_{298}	$(H_T-H_{298})-T(S_T-S_{298})$	H_T-H_{298}	S_T-S_{298}	$(H_T-S_{298})-T(S_T-S_{298})$	H_T-H_{298}	S_T-S_{298}	$(H_T-H_{298})-T(S_T-S_{298})$
Al_2SiO_5 Sillimanite	4470 ± 90	25·0 ± 0·5	6930 ± 140	17·76 ± 0·35	−1950 ± 40	29320 ± 590	48·68 ± 0·97	−19360 ± 380	38450 ± 770	57·19 ± 1·14	−30180 ± 600
Cyanite	3940 ± 90	20·7 ± 0·5	7300 ± 145	18·89 ± 0·38	−2145 ± 50	29290 ± 590	49·35 ± 0·99	−20060 ± 400	38740 ± 775	58·48 ± 1·17	−31440 ± 630
Andalusite	4740 ± 90	27·0 ± 0·5	7410 ± 150	19·25 ± 0·39	−2215 ± 50	30080 ± 600	50·89 ± 1·02	−20810 ± 420	38960 ± 780	59·20 ± 1·18	−32080 ± 640
$Al_2O_3 + SiO_2$	4090 ± 41	22·5 ± 0·3	7160 ± 50	18·15 ± 0·22	−1915 ± 60	29810 ± 300	49·25 ± 0·41	−19440 ± 110	39120 ± 390	57·72 ± 0·47	−30140 ± 170
$CaSiO_3$[53] (Wollastonite)	3340 ± 30	19·6 ± 0·2	4830 ± 100	12·18 ± 0·24	−1260 ± 25	18900 ± 380	31·7 ± 0·63	−12800 ± 250	24790 ± 500	36·98 ± 0·74	−19590 ± 390
$CaO + SiO_2$	3350 ± 50	19·5 ± 0·3	4870 ± 50	12·21 ± 0·21	−1235 ± 55	19910 ± 290	32·74 ± 0·40	−12830 ± 110	26420 ± 400	38·68 ± 0·45	−20000 ± 160
Ca_2SiO_4[55] (Calcium Orthosilicate)	No data	No data	6860 ± 140	16·54 ± 0·33	−1410 ± 30	28360 ± 570	45·71 ± 0·91	−17350 ± 340	37700 ± 750	54·43 ± 1·09	−27620 ± 560
$2CaO + SiO_2$	5030 ± 90	29·0 ± 0·5	7190 ± 100	15·94 ± 0·38	−780 ± 90	28910 ± 470	47·55 ± 0·69	−18640 ± 220	38460 ± 630	55·41 ± 0·80	−28030 ± 330
$CaMgSi_2O_6$ (Diopside)	No data	No data	9470 ± 95	24·06 ± 0·24	−2560 ± 25	37550 ± 380	62·87 ± 0·63	−25320 ± 250	49470 ± 500	74·12 ± 0·74	−39470 ± 390
$CaSiO_3 + MgSiO_3$	6250 ± 60	35·8 ± 0·4	9420 ± 140	23·54 ± 0·39	−2350 ± 55	37450 ± 560	62·54 ± 0·63	−25090 ± 70	49690 ± 750	73·0 ± 1·1	−37910 ± 570
Fe_2SiO_4 (Fayalite)	5440 ± 160	35·4 ± 1·14	7460 ± 220	18·95 ± 0·57	−2015 ± 65	29290 ± 880	49·24 ± 1·48	−19950 ± 600	38540 ± 1160	57·86 ± 1·74	−30890 ± 930
$MgSiO_3$[53, 47] (Clinoenstatite)	2910 ± 30	16·2 ± 0·2	4590 ± 45	11·36 ± 0·11	−1090 ± 10	18550 ± 190	30·8 ± 0·31	−12250 ± 120	24910 ± 250	36·0 ± 0·36	−18290 ± 180
$MgO + SiO_2$	2960 ± 40	16·55 ± 0·2	4560 ± 45	11·60 ± 0·2	−1240 ± 55	18600 ± 260	31·02 ± 0·36	−12420 ± 100	24400 ± 340	36·38 ± 0·41	−19260 ± 150
Mg_2SiO_4[113] (Forsterite)	4180 ± 40	22·7 ± 0·2									
$2MgO + SiO_2$	4250 ± 50	23·1 ± 0·4									
$MnSiO_3$[55] (Rhodonite)	3460 ± 70	21·3 ± 0·3	4830 ± 100	12·34 ± 0·25	−1340 ± 30	19140 ± 380	32·03 ± 0·64	−12890 ± 260			
$MnO + SiO_2$	3650 ± 40	24·4 ± 0·7	4840 ± 28	12·30 ± 0·16	−1310 ± 50	19350 ± 190	32·23 ± 0·24	−12880 ± 50			
Na_2SiO_3 (Sodium Metasilicate)	4550 ± 50	27·2 ± 0·3	6300 ± 130	16·04 ± 0·32	−1720 ± 30	24700 ± 590	41·24 ± 0·82	−16540 ± 230			
$Na_2O + SiO_2$	No data	27·5 ± 1·1	6210 ± 190	15·86 ± 0·57	−1720 ± 100	24540 ± 790	40·93 ± 1·25	−16390 ± 460			
$Na_2Si_2O_5$ (Sodium Disilicate)	6330 ± 100	39·4 ± 0·6	9040 ± 180	23·02 ± 0·46	−2470 ± 50	36320 ± 730	60·33 ± 1·21	−24010 ± 480			
$Na_2O + 2SiO_2$	No data	37·5 ± 1·2	8770 ± 200	22·34 ± 0·67	−2400 ± 140	35460 ± 900	58·90 ± 1·35	−23440 ± 450			

Table II—*(contd.)*

T = 1500° K.			Other Thermal Data	Remarks
H_T-H_{298}	S_T-S_{298}	$(H_T-H_{298})-T(S_T-S_{298})$		
52040 ± 1040 53160 ± 1060 52550 ± 1050 53510 ± 590	67·21 ± 1·34 69·37 ± 1·39 68·86 ± 1·38 68·42 ± 0·54	−48780 ± 970 −50890 ± 1020 −50750 ± 1020 −49120 ± 220		High-temperature data derived from original measurements of Neumann[35] low-temperature data were calculated from C_p values recommended by Kelley[46]: estimated accuracy ± 2%. Sillimanite is the stable form up to 1760° K., where it is said to change to andalusite. At a higher temperature, the latter is said to change to mullite, $3Al_2O_3{\cdot}2SiO_2$, and silica. Neither transition has been firmly established. Cyanite is metastable at all temperatures with respect to sillimanite. C_p curves for andalusite and sillimanite, as reported by Neumann, show distinct humps and intersect twice at 750° and 1200° K. Kelley[47] has smoothed out these irregularities
			Transition β (wollastonite) to α (pseudo-wollastonite) at 1483° K.[85]: $\Delta H_{tr.} \sim 1400$:[129] M.P. α $CaSiO_3$ 1813° K.[88] ΔH_f 13,400[49]	Kelley's[47] high-temperature equation has been selected since the latter results of Southard[113] and Gronow and Schwiete[35] straddle his C_p curve. Up to 700° K. agreement is excellent, but at higher temperature the values diverge: estimated accuracy ± 1%. Heat of fusion by Kelley[49] from binary system $CaSiO_3$/$MgSiO_3$. High- and low-temperature data agree well at 298° K.[52]
			Trans γ to β 948° K. $\Delta H_{tr.}$ 471:[35] β to α 1693° K. $\Delta H_{tr.}$ unknown: α to α′ between 1923 and 2023° K. ΔH unknown: M.P. 2403 ± 20° K.	No low-temperature data: estimated accuracy of Gronow and Schwiete's[35] high-temperature data ± 2%, though these authors claim a much higher accuracy. ΔH_γ to β is derived from these data and does not agree with figure of 1510, derived by Gronow[34] from the data of Johannsen and Thorvaldson[45]
			M.P. 1665° K.[49] ΔH_f 18200[49] uncertain	High-temperature data satisfactory: estimated accuracy ± 1%. No low-temperature data available. Heat of fusion by Kelley[49] from binary system $CaMgSi_2O_6$–$KAlSi_2O_6$
			M.P. 1478° K.[5]	λ pt. at 60° K. largely responsible for uncertainty of ± 1·4 in value of S_{298}. High- and low-temperature data[53, 47] do not agree well at 298° K. C_p curve above 298° K. was obtained by weighting the results of Roth and Bertram[86] and Esser, Averdieck, and Grase[84] in the ratio 2 : 1; estimated accuracy ± 3%
			M.P. (incongruent) 1830° K.[4] ΔH_f 14700[49]	Data[53, 47] satisfactory: estimated accuracy ± 1%. Heat of fusion by Kelley[49] from binary system $CaSiO_3$–$MgSiO_3$
			M.P. 2163° K.[5]	No high-temperature data: low-temperature data by Kelley[51]
34510 ± 690 34740 ± 350	44·65 ± 0·89 44·70 ± 0·3	−32470 ± 650 −32310 ± 100	M.P. (incongruent) 1488° K.[126] ΔH_f 8200[49] (uncertain)	Low- and high-temperature C_p data[53, 111] do not agree well at 298° K., and it has been necessary to draw an arbitrary but continuous C_p curve to join the two sets of data smoothly: estimated accuracy ± 2%. Heat of fusion by Kelley[49] from $MnSiO_3$–$MgSiO_3$ and $MnSiO_3$–$MnTiO_3$ binary systems
			M.P. 1361° K.[83] ΔH_f12470[83]	Data[83, 16] satisfactory: estimated accuracy ± 2%. This is the only silicate for which a reliable directly measured heat of fusion is available
			M.P. 1147° K.[82] ΔH_f 8460[49]	Data[83, 46] satisfactory: estimated accuracy ± 2%. Naylor[83] was unable to determine heat of fusion directly, owing to glass formation: value given is by Kelley[49] from binary system $Na_2Si_4O_9$–$NaAlSiO_4$. Naylor[83] also measured C_p of liquid $Na_2Si_2O_5$

Table III

THERMAL DATA FOR BORATES

Borate	$H_{298}-H_0$	S_{298}	T = 500° K.			T = 1000° K.			T = 1200° K.			Other Thermal Data	Remarks
			H_T-H_{298}	S_T-S_{298}	$(H_T-H_{298})-T(S_T-S_{298})$	H_T-H_{298}	S_T-S_{298}	$(H_T-H_{298})-T(S_T-S_{298})$	H_T-H_{298}	S_T-S_{298}	$(H_T-H_{298})-T(S_T-S_{298})$		
$Ca_2B_2O_5$	7500 ± 80	43·9 ± 0·3	10520 ± 110	26·79 ± 0·27	−2880 ± 30	41300 ± 410	69·06 ± 0·69	−27760 ± 280	54720 ± 550	81·28 ± 0·81	−42820 ± 430	M.P. 1760° K.[17] ΔH_f 35490[17]	Data[44, 17] satisfactory: estimated accuracy ± 1%
$3CaO + B_2O_3$	7320 ± 130	41·54 ± 0·7	10600 ± 180	26·58 ± 0·43	−2690 ± 40	50870 ± 780	79·64 ± 1·23	−28770 ± 450	66070 ± 1020	93·62 ± 1·46	−46270 ± 730		
$Ca_2B_2O_5$	5870 ± 60	34·7 ± 0·2	8310 ± 60	21·11 ± 0·21	−2250 ± 20	34860 ± 350	57·32 ± 0·57	−22460 ± 220	45840 ± 460	67·33 ± 0·67	−34960 ± 350	M.P. 1585° K.[17] ΔH_f 24090[17] α to β transition at 804° K.,[17] $\Delta H_{tr.}$ 1100	Data as for $3CaO.B_2O_3$: m.p. recommended by National Bureau of Standards is 1571° K.
$2CaO + B_2O_3$	5630 ± 90	32·04 ± 0·5	8290 ± 130	20·85 ± 0·27	−2130 ± 30	41880 ± 600	64·83 ± 0·94	−22950 ± 340	54030 ± 780	76·02 ± 1·11	−37190 ± 550		
CaB_2O_4	4130 ± 40	25·1 ± 0·2	5950 ± 60	15·09 ± 0·15	−1600 ± 20	24410 ± 240	40·35 ± 0·40	−15940 ± 160	32630 ± 330	47·84 ± 0·48	−26780 ± 250	M.P. 1435° K.[17] ΔH_f 17670[17]	Data as for $3CaO.B_2O_3$: m.p. recommended by National Bureau of Standards is 1427° K.
$CaO + B_2O_3$	3950 ± 60	22·54 ± 0·3	5980 ± 80	15·12 ± 0·20	−1580 ± 20	32890 ± 420	50·02 ± 0·65	−17130 ± 230	41990 ± 540	58·42 ± 0·76	−28110 ± 370		
CaB_4O_7	5590 ± 60	32·2 ± 0·3	9500 ± 100	24·03 ± 0·24	−2520 ± 30	40870 ± 410	66·94 ± 0·67	−26070 ± 260	54920 ± 550	79·74 ± 0·80	−40770 ± 410	M.P. 1260° K.[17] ΔH_f 27060[17]	Data as for $3CaO.B_2O_3$: heat of fusion was determined via heats of solution because of glass formation
$CaO + 2B_2O_3$	6200 ± 80	35·58 ± 0·4	9650 ± 120	24·51 ± 0·30	−2610 ± 30	56790 ± 660	85·23 ± 1·01	−28440 ± 350	71940 ± 840	99·24 ± 1·17	−47710 ± 560		

$(2CaO + Fe_2O_3 = Ca_2Fe_2O_5)$.

Accuracy *C*

$\Delta G^\circ_{1000-1400^\circ K.} = -16{,}000$

This equation was calculated by compounding the equation for the reduction of the dicalcium ferrite to iron with the following :

(*a*) $\frac{3}{2}Fe + O_2 = \frac{1}{2}Fe_3O_4$,

$\Delta G^\circ_{298-833^\circ K.} = -132{,}300 + 37{\cdot}8\,T$

(*b*) $4Fe_3O_4 + O_2 = 6Fe_2O_3$,

$\Delta G^\circ_{1000-1730^\circ K.} = -109{,}000 + 61{\cdot}8\,T$

Equation (*a*) is based on the results of Emmett and Shultz,[23] and is now preferred to that cited in Part I.[94] It has to be extrapolated considerably for use here, since the equilibrium cannot be studied above 570° C. Values of ΔG° for equation (*a*) may also be calculated from the equation given by Kelly,[50] and from the Fe_3O_4–wüstite–Fe studies by Darken and Gurry,[19,20] In the temperature range of interest here the differences are greatest at 1400° C., where Kelley's value is 1 kg.cal. and that of Darken and Gurry is ½ kg.cal. more negative than the value derived from the equation recommended. The latter is preferred because Kelley's equation relies on the extrapolation of indifferent thermal data, and the calculations from Darken and Gurry's results are indirect.

Equation (*b*) is based on the results of Darken and Gurry,[19, 20] as recommended by Richardson and Jeffes.[92]

The value of ΔS°, obtained from these equations, is + 10 cal./degree. This seems unreasonably large but allowing for the errors which may arise in compounding the three equations, it is not likely to be significant. A temperature-dependent term is not, therefore, shown in the recommended ΔG° equation.

Monocalcium Ferrite $(CaO + Fe_2O_3 = CaFe_2O_4)$

Honus[38, 40] has calculated the heat of this reaction from Marchal's data[74] on the sulphur dioxide and oxygen pressures developed on heating $CaSO_4$ with and without Fe_2O_3. Examination of Marchal's data shows her results to have been inadequate for such a calculation, and the figure proposed by Honus is, therefore, not included.

Fayalite $(2Fe + O_2 + SiO_2 = Fe_2SiO_4)$.

Accuracy *B*

$\Delta G^\circ_{298-1478^\circ K.} = -135{,}300 + 34{\cdot}4\,T$

The oxidation reduction equilibrium of fayalite with CO/CO_2 gas mixtures has been studied by Schenck, Franz, and Laymann,[103] and partic-

ularly by Cirilli.[15] The equilibrium has been approached from the CO-rich side only and the results may, therefore, be open to the objection raised under ferrous aluminate (*see* page 223). The manner in which calculations from these results agree with those from other data quoted subsequently suggests, however, that such an objection may not apply in this case. The reduction results agree, and have been combined with the data on CO,CO_2,O_2 equilibrium cited in Part I[94] to obtain values of ΔG° for this reaction. Since the temperature range covered by these investigations is only 200°, the slope of the plot of ΔG° against temperature has been deduced from the value of $\Delta S^\circ_{1200^\circ K.}$ calculated from the following thermal data: entropies of Fe and O_2 from Kelley;[48, 46] entropies of SiO_2 from Mosesman and Pitzer;[77] entropy of Fe_2SiO_4 at 25° C. from Kelley;[46] specific heat of Fe_2SiO_4 above 25° C. from a weighted average of the results of Roth and Bertram,[96] and of Esser, Averdieck and Grass[24] giving $\Delta S^\circ_{1200^\circ K.} = 93{\cdot}3 \pm 3$.

$(2x\text{Fe} + 2\text{Fe}_{1-x}\text{O} + \text{SiO}_2 = \text{Fe}_2\text{SiO}_4)$. Accuracy *B*

$$\Delta G^\circ_{843\text{–}1478^\circ K.} = -9600 + 3{\cdot}7\,T$$
$$\Delta G^\circ_{1478\text{–}1644^\circ K.} = +8130 - 8{\cdot}3\,T$$
$$\Delta G^\circ_{1644\text{–}1808^\circ K.} = -6470 + 0{\cdot}6\,T$$
$$\Delta G^\circ_{1808\text{–}1986^\circ K.} = -6830 + 0{\cdot}8\,T$$
$$\Delta G^\circ_{1986^\circ K.} = -8930 + 1{\cdot}86\,T$$

The reaction between silica and wüstite to form fayalite requires the addition of free iron, because of the oxygen-rich non-stoichiometry of wüstite. This varies with temperature and is, therefore, represented by the term $(1-x)$ in the chemical equation. The ΔG° equations for this reaction were calculated from the equation already given for the reduction of fayalite to iron, the first two equations given under wüstite, and the following heats of fusion: SiO_2, — 2100 cal. at 1713° C. (Mosesman and Pitzer[77]); Fe_2SiO_4, — 17,730 cal. at 1205° C. (from an estimated entropy of melting of about 12 cal./degree); and Fe, — 3560 cal. at 1535° C. (Kelley[48]). This extrapolation is only approximate, but it is interesting, as it can be used to provide information on activities in a molten slag of the composition corresponding to fayalite. (*See* page 220).

Ferrous Silicate $(x\text{Fe} + \text{Fe}_{1-x}\text{O} + \text{SiO}_2 = \text{FeSiO}_3)$

A value of — 2·8 kg.cal. (Accuracy *A*) was calculated for $\Delta G^\circ_{1873^\circ K.}$ for the formation of liquid $FeSiO_3$ from liquid wüstite, liquid iron, and liquid silica, from the activities of silica and wüstite in a melt corresponding to the composition $FeSiO_3$. The activity of the silica was determined

Table IV
THERMAL DATA FOR SPINELS

Spinel	$H_{298}-H_0$	S_{298}	$T = 500^\circ K.$			$T = 1000^\circ K.$			$T = 1500^\circ K.$			Other Thermal Data	Remarks
			H_T-H_{298}	$ST-S_{298}$	$(H_T-H_{298})-T(ST-S_{298})$	H_T-H_{298}	$ST-S_{298}$	$(H_T-H_{298})-T(ST-S_{298})$	H_T-H_{298}	$ST-S_{298}$	$(H_T-H_{298})-T(ST-S_{298})$		
Fe_3O_4	5770 ± 120	35·0 ± 0·7	8430 ± 170	21·5 ± 0·43	−2320 ± 50							M.P. 1870° K. ΔH_f 33000 ± 2000[19]	Low- and high-temperature data[46, 47] do not agree well at 298° K.; Millar[14] has reported a 'hump' in the C_p curve at 114° K., which Kelley[46] has smoothed out; estimated accuracy of C_p data ± 2°. There are no C_p data above 1100° K. and extrapolation beyond this temperature is very uncertain
$FeCr_2O_4$	5360 ± 50	34·9 ± 0·4	7090 ± 70	18·03 ± 0·18	−1930 ± 20	27890 ± 280	46·84 ± 0·47	−18950 ± 190					Data[100, 11] satisfactory; estimated accuracy above 298° K. ± 1%. 'Humps' in the low-temperature C_p curve at 75 and 135° K. make the extrapolation below 53° K. rather uncertain, and account for the error limit of ± 0·4 in S_{298}
$MgCr_2O_4$	4450 ± 40	25·3 ± 0·2	7150 ± 70	17·86 ± 0·18	−1780 ± 20	27850 ± 280	46·04 ± 0·46	−18490 ± 180	49550 ± 500	63·76 ± 0·64	−46090 ± 460		Data satisfactory[100, 101]; estimated accuracy ± 1°.
$MgO+Cr_2O_3$		25·95 ± 0·45	7540 ± 100	19·64 ± 0·25	−2270 ± 40	27920 ± 350	47·89 ± 0·61	−19970 ± 260	49550 ± 630	65·25 ± 0·83	−48330 ± 610		

Table V—THERMAL DATA FOR OTHER COMPOUNDS

Other Compound	$H_{298}-H_0$	S_{298}	$T = 500°$ K.			$T = 1000°$ K.		
			H_T-H_{298}	S_T-S_{298}	$(H_T-H_{298})-T(S_T-S_{298})$	H_T-H_{298}	S_T-S_{298}	$(H_T-H_{298})-T(S_T-S_{298})$
$CaAl_2O_4$	No data	No data	7000 ± 70	16·7 ± 0·17	−1350 ± 20	27300 ± 270	45·32 ± 0·45	−18020 ± 180
$CaO + Al_2O_3$	4130 ± 60	22·0 ± 0·35	6910 ± 90	17·4 ± 0·23	−1790 ± 20	27880 ± 370	46·13 ± 0·61	−18250 ± 240
$Ca_3Al_2O_6$	No data	No data	11000 ± 110	28·44 ± 0·28	−3220 ± 30	43100 ± 430	72·11 ± 0·72	−29010 ± 290
$3CaO + Al_2O_3$	7500 ± 130	41·0 ± 0·75	11540 ± 190	28·86 ± 0·46	−2890 ± 50	45870 ± 730	75·75 ± 1·2	−29880 ± 470
$Ca_3P_2O_8$	9260 ± 100	56·40 ± 0·4	12340 ± 250	33·02 ± 0·66	−4180 ± 80	50640 ± 1130	85·67 ± 1·71	−35040 ± 580
$3CaO + P_2O_5$	No data	No data	12870 ± 260	32·19 ± 0·63	−3230 ± 60	60350 ± 1540	99·06 ± 2·51	−38720 ± 970
$CaTiO_3$	3840 ± 40	22·4 ± 0·1	5430 ± 50	13·86 ± 0·14	−1500 ± 20	20380 ± 200	34·48 ± 0·35	−14100 ± 150
$CaO + TiO_2$	33760 ± 60	21·51 ± 0·25	5410 ± 80	13·66 ± 0·19	−1420 ± 20	20140 ± 300	34·52 ± 0·49	−14370 ± 200
$FeTiO_3$	4060 ± 40	25·3 ± 0·3	5330 ± 50	13·56 ± 0·14	−1450 ± 20	20440 ± 200	34·34 ± 0·34	−13900 ± 140
$MgTiO_3$	3280 ± 30	17·8 ± 0·1	5130 ± 50	13·07 ± 0·13	−1410 ± 10	19800 ± 200	33·27 ± 0·33	−13470 ± 130
$MgO + TiO_2$	3370 ± 60	18·56 ± 0·20	5100 ± 70	13·05 ± 0·18	−1430 ± 20	19330 ± 270	32·81 ± 0·47	−13480 ± 200

from the FeO–SiO_2 phase diagram, and the activity of the ferrous oxide from the measurements of Taylor and Chipman.[117]

The work of Sahama and Torgeson[102] suggests that $\Delta G°_{800° K.}$ for the solid reaction $Fe_2SiO_4 + SiO_2 = 2FeSiO_3$ may be of the order of + 1 kg.cal. When this value is compounded with the corresponding $\Delta G°$ for the formation of fayalite from its oxides, calculated from an extrapolation of the fayalite equation already given, a value of about − 2½ kg.cal. (Accuracy *B*) is obtained for the free energy of formation of solid $FeSiO_3$ at 800° K. This is not incompatible with the value given above for molten $FeSiO_3$ when allowance is made for the likely breaks in the free-energy temperature curve caused by changes of states.

Ilmenite ($2Fe + 2TiO_2 + O_2 = 2FeTiO_3$). Accuracy *B*

$$\Delta G°_{1173-1400° K.} = -129{,}220 + 25{\cdot}86\ T$$

Shomate, Naylor, and Boericke[111] have measured the equilibrium between H_2/H_2O gas mixtures, and the solids Fe, TiO_2, and $FeTiO_3$, between 950° and 1100° C. Their results are probably affected by thermal segregation in the gases, owing to the slow rate of flow in their apparatus. They were, therefore, plotted on a $\Delta G°/T$ plot ; a line was drawn through the lower temperature results, where thermal segregation should be at a minimum, with a slope equal to $-\Delta S°_{1200° K.}$ (25·8 cal./degree) calculated from the heat-capacity data. The equilibrium studied was approached from the oxidation and the reduction sides. A small systematic difference in the results occurred, according to the direction of approach to equilibrium. It is thought that this may be due to a particle-size phenomenon of the type discussed under ferrous aluminate (page 223), but the observed discrepancy was far less. The equation recommended for this line gives $\Delta G°$ values 1 kg.cal. more negative at 1100° C. than those obtained by Shomate, Naylor, and Boericke.[111]

($Fe_{0·95}O + 0·05Fe + TiO_2 = FeTiO_3$). Accuracy *B*

$$\Delta G°_{1173-1400° K.} = -1770 - 2{\cdot}40\ T$$

This equation for the reduction of ilmenite to free iron was compounded with that for the reduction of ferrous oxide, quoted under fayalite. (*See* page 229).

Wüstite ($2(1-x)\ Fe + O_2 = 2Fe_{1-x}O$)

$\Delta G°_{848-1644° K.} = -125{,}700 + 30{\cdot}69\ T$. Accuracy *A*

$\Delta G°_{1644-1808° K.} = -111{,}100 + 21{\cdot}81\ T$. Accuracy *B*

$\Delta G°_{1808-2000° K.} = -118{,}100 + 25{\cdot}71\ T$. Accuracy *B*

Table V—*(contd.)*

T = 1200° K.			Other Thermal Data	Remarks
H_T-H_{298}	S_T-S_{298}	$(H_T-H_{298})-T(S_T-S_{298})$		
36000 ± 360	53·24 ± 0·53	−27890 ± 280	M.P. 1808° K.[88]	Data from Gronow and Schwiete,[25] who claim a high degree of accuracy which is difficult to accept, since their data for CaO and Al_2O_3, obtained in the same series of experiments, do not agree with those of other workers. In the absence of confirmatory data for the aluminate the accuracy has been estimated as ± 1%
36780 ± 490	54·24 ± 0·72	−28310 ± 380		
56200 ± 560	84·44 ± 0·84	−45130 ± 450	M.P. 1873° K.[88]	Data are those of Gronow and Schwiete[25] and the remarks on data for $CaAl_2O_4$ are equally applicable: estimated accuracy ± 1%
60860 ± 970	89·44 ± 1·43	−46470 ± 750		
68400 ± 1560	102·9 ± 2·06	−55080 ± 910	M.P. 2003° K.[125] Transition β to α between 1523 and 1773° K.[125] $\Delta H_{tr.}$ 4500	C_p data from Britzke and Vesselovskii,[9] who state that transition β to α takes place between 1368 and 1398° K., and that heat of transition is 4500. Trömel and Schneiderhöhn[125] place the transition temperature between 1523 and 1773° K. Low-temperature data are by Southard and Milner[114]
76720 ± 1920	113·35 ± 2·87	−59300 ± 1520		
26640 ± 270	40·18 ± 0·4	−21580 ± 210	Transition α to β at 1530° K.[84] $\Delta H_{tr.}$ 550[84]	Data[107, 84] satisfactory: estimated accuracy ± 1%
27240 ± 550	40·56 ± 0·58	−21430 ± 150		
T = 1500° K.				
36920 ± 370	47·67 ± 0·48	−34590 ± 150	M.P. 1640° K.[84] ΔH_f 21670[84]	Data[107, 84] satisfactory: estimated accuracy ± 1% M.P. doubtful, as indications of melting at about 1450° C. have been reported[84]
35660 ± 360	46·09 ± 0·46	−33480 ± 330		Data[107, 84] satisfactory: estimated accuracy ± 1%
34420 ± 480	44·87 ± 0·63	−32890 ± 460		

The work of Darken and Gurry[19, 20] and other work, as cited under Iron in the Appendix of Part I,[94] indicates that, within the error limits, the free-energy equations for the formation of wüstite from iron and oxygen are linear, in spite of the nonstoichiometry of the iron oxide. The data has been re-assessed since Part I was written, and the equations given above are now recommended. The value of x in the chemical equation is very nearly 0·05 for solid wüstite above 900° C.

Lithium

Silicate ($Li_2O + SiO_2 = Li_2SiO_3$). Accuracy *D*

$$\Delta H^\circ_{298^\circ K.} = -24{,}600$$

Kröger and Fingas[64] have measured the CO_2 pressure developed on heating a mixture of Li_2CO_3 and SiO_2, and on heating Li_2CO_3 alone. The experimental points for the reaction $Li_2CO_3 + SiO_2 = Li_2SiO_3 + CO_2$, plotted as ΔG° against T, were fitted to the best straight line with a slope of 35·7 cal./degree through them. This slope is that of the analogous reaction involving sodium compounds and gave a value of $\Delta H^\circ_{700^\circ K.} = 29{,}600$ cal. On the assumption that $\Delta H^\circ_{298^\circ K.} = \Delta H^\circ_{700^\circ K.}$ this can be combined with de Forcrand's[28] value of − 54,200 for $\Delta H^\circ_{298^\circ K.}$ for the reaction $Li_2O + CO_2 = Li_2CO_3$, giving $\Delta H^\circ_{298^\circ K.} = -24{,}600$ for the formation of the silicate from its constituent oxides. It was decided to do this rather than use the data of Kröger and Fingas for the CO_2 pressure developed on heating Li_2CO_3 alone, as their experimental points are very scattered.

The entropy of Li_2SiO_3 is not known, and a free-energy equation cannot, therefore, be recommended. The value of $\Delta G^\circ_{298^\circ K.}$, shown in Fig. 1, is based on the assumption that $\Delta S^\circ_{298^\circ K.}$ is negligible, as in the analagous reactions for Na_2SiO_3.

Magnesium

Aluminate ($2MgO + 2Al_2O_3 = 2MgAl_2O_4$). Accuracy *C*

$$\Delta G^\circ_{1673^\circ K.} = -10{,}000$$

Lovell, Rigby, and Green[68] have calculated, by microscopic studies, an equilibrium constant in terms of concentrations for the solid reaction $MgO + FeAl_2O_4 = MgAl_2O_4 + 0{\cdot}05\ Fe + Fe_{0{\cdot}95}O$ at 1400° C. Their results lead to a value of $\Delta G^\circ_{1673^\circ K.}$ for their reaction—equal to − 0·2 kg.cal. This was compounded with the data for the formation of $FeAl_2O_4$ from its component oxides. (*See* page 223.)

Chromite ($MgO + Cr_2O_3 = MgCr_2O_4$). Accuracy *B*

$$\Delta G^\circ_{1673^\circ K.} = -4000$$

Lovell, Rigby, and Green[68] have calculated, by microscopic studies, an equilibrium constant in terms of concentrations for the solid reaction $MgO + FeCr_2O_4 = MgCr_2O_4 + 0{\cdot}05Fe + Fe_{0{\cdot}95}O$ at 1400° C. Their results lead to a value of $\Delta G^\circ_{1673^\circ K.}$ for their reaction of + 4·2 kg.cal. This was compounded with the data for the formation of $FeCr_2O_4$ from its component oxides. (*See* page 224).

Silicates

Clinoenstatite ($MgO + SiO_2 = MgSiO_3$). Accuracy *A*

$$\Delta G^\circ_{298\text{–}1600^\circ K.} = -8900 + 1{\cdot}1\,T$$

Torgeson and Sahama[123] have measured the heats of solution of $Mg(OH)_2$, quartz, and clinoenstatite in 20% HF at 73·7° C., and of MgO and $Mg(OH)_2$ in *N* HCl. Because MgO dissolves in HF only with difficulty, they have calculated its heat of solution from their heat of solution of $Mg(OH)_2$ in HF and the difference between their heats of solution of $Mg(OH)_2$ and MgO in HCl. In this way they have deduced a value of — 8690 cal. for ΔH° for the formation of the silicate, which is probably accurate to ± 500 cal.

Forsterite ($2MgO + SiO_2 = Mg_2SiO_4$). Accuracy *B*

$$\Delta G^\circ_{298\text{–}1700^\circ K.} = -15{,}120 - 0{\cdot}0\,T$$

Torgeson and Sahama[123] have measured the heats of solution of $Mg(OH)_2$ and SiO_2 in 20% HF at 73·7° C. They were unable to obtain pure forsterite, but they measured the heats of solution of seven solid solutions of forsterite and fayalite. These compounds, ranging from 0 to 90·5% of forsterite, showed heats of solution which varied linearly with the molar composition, and which could, therefore, be safely extrapolated to 100% of forsterite. They determined the heat of formation of MgO from $Mg(OH)_2$ from the difference between the heats of solution of the oxide and hydroxide in *N* HCl. They thus obtained a value of — 15,120 cal. for $\Delta H^\circ_{298^\circ K.}$ for the formation of forsterite. This is thought to be reliable to ± 500 cal. The free-energy equation is based on ΔS°_{298}, which is equal to — 0·4 ± 0·6 cal./degree. No heat-capacity data are available for forsterite above 25° C.

The equilibrium $2MgO + Fe_2SiO_4 = Mg_2SiO_4 + 0{\cdot}1Fe + 2Fe_{0{\cdot}95}O$ has been investigated by Lovell, Rigby, and Green,[68] who made microscopic studies of the solid solutions obtained on heating MgO and Fe_2SiO_4 in contact with iron. They obtained an equilibrium constant in terms of molar concentrations equal to 0·025 at 1400° C. It is almost certain that both the systems Fe_2SiO_4–Mg_2SiO_4 and MgO–FeO behave ideally (*see* page 220), so that this equilibrium constant may be used to calculate the value of $\Delta G^\circ_{1673^\circ K.}$ for their reaction as — 12,300 cal. When compounded with $\Delta G^\circ_{1673^\circ K.}$ for the formation of solid fayalite from its component oxides (— 3400), by extrapolation of the free-energy curve for solid fayalite beyond its melting point, a value of — 15,700 is obtained for the corresponding free energy of formation of forsterite. This agrees closely with the equation recommended here, and justifies its representation by a full line in Fig. 2.

Schneider and Hesse[104] have measured the magnesium pressures in the equilibrium: $4MgO + Si = 2Mg_{(gas)} + Mg_2SiO_4$ by an entrainment technique, and have identified the Mg_2SiO_4 by X-rays. Their results, however, lead to values for the free energy of formation of forsterite which are approximately double those recommended here, and it is considered that more reliance should be placed on the heat of solution data than on their results.

Manganese

Silicates

Rhodonite ($MnO + SiO_2 = MnSiO_3$). Accuracy *C*

$$\Delta G^\circ_{298\text{–}1600^\circ K.} = -7100 + 3{\cdot}0\,T$$

Three significant determinations have been made of the heat of this reaction. Le Chatelier's[12] result of — 2700 cal. was obtained by firing a mixture of MnO, SiO_2 and carbon in a bomb calorimeter. Wologdine[132] and Wologdine and Penkiewitsch[133] have measured the heat of reaction $MnCO_3 + SiO_{2\ (quartz)} = MnSiO_3 + CO_2$ in a bomb calorimeter. They have used Le Chatelier's[12] value of the heat of the reaction $MnO + CO_2 = MnCO_3$ to obtain a value of — 7725 cal. for the heat of formation of rhodonite from its oxides. Mulert[78] has measured the heat of solution, in 20% of HF, of rhodonite and quartz, but not of MnO. Using auxiliary data from other sources, he has calculated $\Delta H^\circ_{298^\circ K.}$ to be — 6500 cal. The mean of Wologdine's and Mulert's value was used in the recommended equation.

Some information is available on liquid $MnSiO_3$ at 1600° C. Körber and Oelsen[59, 60] have shown that the silica saturation limit in the system MnO–SiO_2 is about 54 mol. per cent. This means that the activity of solid silica in the melt, corresponding to the composition $MnSiO_3$, is nearly unity, and Rey[90] has calculated a value of about 0·8 from the MnO–SiO_2 phase diagram. Körber and Oelsen have also measured the equilibrium [Mn] + (FeO) = (MnO) + [Fe], where the manganese is in liquid iron, and the manganese and iron oxides are in liquid slag. They have further shown that, when this slag is saturated with silica, the equilibrium is shifted in favour of the (MnO) by a factor of about six. It is known that the liquid system FeO–MnO is ideal with respect to the two oxides, and it is reasonable to expect the liquid system $MnSiO_3$–"$FeSiO_3$" to behave ideally with respect to the two liquid silicates. It is also known from the work of Taylor and Chipman[117] that the activity coefficient of ferrous oxide, relative to the pure liquid phase, is approximately unity in liquid "$FeSiO_3$." The corresponding activity coefficient of manganese is, therefore, of the order of 1/6. It follows that $\Delta G^\circ_{1873^\circ K.}$ for the formation of liquid $MnSiO_3$ from liquid MnO and solid silica is — 10,000 cal. This value is approximately 5 kg.cal. more negative than that which might reasonably be expected from the equation given for the free energy of formation of the solid silicate from the solid oxides, when allowance is made for the effects of the changes of state. The cause of the discrepancy is not known.

Potassium

Silicate ($K_2O + SiO_2 = K_2SiO_3$). Accuracy *D*

$$\Delta H^\circ_{298^\circ K.} = -63{,}000$$

The only data available are those of Kröger and Fingas,[63] who measured the CO_2 pressures developed on heating mixtures of potassium carbonate and quartz at temperatures between 450 and 570° C. Great difficulty was experienced in obtaining equilibrium, and the results show a serious scatter when plotted as $-RT \ln p_{CO_2}$ against T. It was assumed, therefore, that the entropy change for this reaction is the same as for the corresponding reaction between the carbonate and silicate of sodium ($\Delta S°_{298°K.} = -35{\cdot}7$ cal./degree), and the best straight line with this slope was drawn through the experimental points. This line leads to an approximate value of + 31,000 cal. for $\Delta H°$. When this result was combined with de Forcrand's[28] value of − 94,260 for $\Delta H°_{298°K.}$ for the reaction $K_2O + CO_2 = K_2CO_3$, a value of − 63,000 cal. was obtained for $\Delta H°$ for the formation of the silicate from potassium oxide and quartz. The free-energy line in Fig. 1 was plotted on the assumption that the $\Delta S°$ is the same as for the corresponding sodium reaction.

Leucite ($K_2O + Al_2O_3 + 4SiO_2 = K_2O.Al_2O_3.4SiO_2$). Accuracy *D*

$$\Delta H°_{298°K.} = -102{,}000$$

Mulert[79] measured the heats of solution of leucite and silica in 20% HF. He also measured the heats of solution of a series of hydrated aluminas in 20% HF and extrapolated those values to 0% H_2O. He *calculated* the heat of solution of K_2O in 20% HF from Thomsen's values[118] for the heats of solution of K_2O in water and the heat of neutralization of KOH solution by 20% HF. From these he obtained − 101,800 cal. for the heat of formation of leucite from its component oxides. Because of the uncertainty in the calculation of the heat of solution of K_2O in 20% HF, the accuracy grading is *D*.

Sodium

Silicate ($Na_2O + SiO_2 = Na_2SiO_3$) Accuracy *C*

$$\Delta G°_{298\text{–}1361°K.} = -55{,}550 - 1{\cdot}40\,T$$

$$\Delta G°_{1361\text{–}1600°K.} = -43{,}080 - 10{\cdot}55\,T$$

Although there is a fair amount of data on Na_2SiO_3 which has been reviewed by McCready,[70] it is considered that the only work on which reliance can be placed is that of Troitzsch.[126] By heat of solution experiments in 20% HF he obtained a value of −20,380 cal. for $\Delta H°_{298°K.}$ for the reaction $Na_2CO_3 + SiO_{2(quartz)} = Na_2SiO_3 + CO_2$. This result was combined with de Forcrand's[28] value of − 76,880 cal. for $\Delta H°_{298°K.}$ for the reaction $Na_2O + CO_2 = Na_2CO_3$, to obtain a value of − 56,500 cal. for $\Delta H°_{298°K.}$ for the formation of the silicate from sodium oxide and silica.

Phosphate ($3Na_2O + P_2O_5 = 2Na_3PO_4$). Accuracy *D*

$$\Delta H°_{298°K.} = -264{,}000$$

Use was made of the following heats of reaction :

(*a*)[2] $3NaOH_{(aq.)} + H_3PO_{4(aq.)} = Na_3PO_{4(aq.)} + 3H_2O$

$$\Delta H°_{298°K.} = -33{,}600$$

(*b*)[29] $\frac{1}{2}P_2O_5 + \frac{3}{2}H_2O + aq. = H_3PO_{4(aq.)}$

$$\Delta H°_{298°K.} = -27{,}200$$

(*c*)[89] $Na_2O + aq. = 2NaOH_{(aq.)}$

$$\Delta H°_{298°K.} = -56{,}500$$

(*d*) $Na_3PO_4 + aq. = Na_3PO_{4(aq.)}$

$$\Delta H°_{298°K.} = -13{,}000$$

Equation (*d*) is an estimate based on the measured heats of solution in water of $Na_3PO_4.12H_2O$. $Na_2HPO_4.12H_2O$, and Na_2HPO_4, quoted by Landolt-Börnstein-Scheel,[65] on the assumption that the difference between the heats of solution of $Na_3PO_4.12H_2O$ and the anhydrous compound is the same for the corresponding disodium compounds. These equations combine to give the ΔH value heading the paragraph. The dotted free-energy line in Fig. 3 was drawn on the assumption that $\Delta S°_{298°K.}$ is negligible ; the break at 358° C. is caused by the sublimation of solid P_2O_5.

ADDENDUM*

Since this paper was written some further important thermal measurements, which have just been made at the U.S. Bureau of Mines Pacific Station, have been brought to the authors' notice by Dr. K. K. Kelley. These are as follows :

S_{298} (Cyanite) 20·02 ± 0·08 cal./degree

S_{298} (Andalusite) 22·3 ± 0·1 cal./degree

S_{298} (Sillimanite) 23·0 ± 0·1 cal./degree

$$MnO_{(s)} + SiO_{2\,(qnartz)} = MnSiO_{3(s)}$$

$$\Delta H_{298} = -5920 \pm 170$$

In the opinion of the authors these data are so much more reliable than the corresponding data cited in the Appendix and the Tables, that the silicate diagram (Fig. 1) has been amended accordingly.

It is interesting to compare the new heat of formation of rhodonite given above, with a corresponding value for tephroite (Mn_2SiO_4) of − 11·3 kg.cal., which has just been determined by one of us (J.H.E.J.).

* Received 10th October, 1950.

References and Bibliography

1. C. T. Anderson : *Journal of the American Chemical Society*, 1937, vol. 59, p. 488.
2. M. Berthelot and Lougwinine : *Annales de Chimie et de Physique*, Series 5, 1876, vol. 9, p. 23.
3. F. S. Boericke and W. M. Bangert : *United States Bureau of Mines*, 1945, Report No. 3813.
4. N. L. Bowen and O. Anderson : *American Journal of Science*, 4th Series, 1914, vol. 37, p. 488.
5. N. L. Bowen and J. F. Schairer : *Ibid.*, 5th Series, 1932, vol. 24, p. 200.
6. W. L. Bragg : " Atomic Structure of Minerals," 1937, Cornell University Press.
7. E. Brandenburger : " Symposium on Cement," 1937 : Stockholm.
8. V. Britzke and V. K. Veselovskii : *Izvestia Akad. Nauk. U.S.S.R.* Otdel, Tekh. Nauk. 1937, vol. 4, p. 479.
9. E. N. Bunting : *Journal of Research of the National Bureau of Standards*, 1931, vol. 6, No. 6, p. 948.
10. E. N. Bunting, *Ibid.*, 1933, vol. 11, p. 725.
11. E. G. Bunzel and E. J. Kohlmeyer : *Zeitschrift für anorganische und allgemeine Chemie*, 1947, vol. 254, p. 1.
12. A. Le Chatelier : *Comptes Rendus*, 1896, vol. 122, p. 80.
13. J. Chipman : *Discussions of the Faraday Society*, 1948, vol. 4, p. 23.
14. J. Chipman, J. B. Gero and T. B. Winkler : *Journal of Metals*, 1950, *Technical Publication No.* 2776*C*.
15. V. Cirilli : *Gazzetta Chimica Italiana*, 1946, vol. 76, p. 331.
16. V. Cirilli, *Ibid.*, 1946, vol. 76, p. 339.

17. V. CIRILLI, *Ricerca Scientifica e Ricostruzione*, 1947, vol. 17, No. 6, p. 3.
18. S. S. COLE and N. W. TAYLOR : *Journal of the American Ceramic Society*, 1935, vol. 18, p. 55.
19. L. S. DARKEN and R. W. GURRY : *Journal of the American Chemical Society*, 1946, vol. 68, p. 798.
20. L. S. DARKEN and R. W. GURRY, *Ibid.*, 1939, vol. 61, p. 2407.
21. H. C. J. DE DECKER : *Recueil des Travaux Chimiques des Pays-Bas*, 1941, vol. 60, p. 413.
22. W. EITEL and H. RICHTER : *Zement*, 1942, vol. 31, p. 505.
23. P. H. EMMETT and J. F. SHULTZ : *Journal of the American Chemical Society*, 1933, vol. 55, p. 1376.
24. H. ESSER, R. AVERDIECK, and W. GRASS : *Archiv für das Eisenhüttenwesen*, 1933, vol. 6, p. 289.
25. R. FAIVRE and G. CHAUDRON : *Comptes Rendus*, 1948, vol. 226, p. 249.
26. A. FINKELSTEIN : *Chemische Berichte*, 1906, vol. 39, p. 1585.
27. H. FLOOD, T. FÖRLAND, and B. ROALD : *Journal of the American Chemical Society*, 1949, vol. 71, p. 572.
28. M. DE FORCRAND : *Comptes Rendus*, 1908, vol. 146, p. 511.
29. M. FRANDSEN : *Journal of Research of the National Bureau of Standards*, 1933, vol. 10, p. 35.
30. R. FRICKE and G. WEITBRECHT : *Zeitschrift für Elektrochemie*, 1942, vol. 48, p. 87.
31. J. W. GREIG : *American Journal of Science*, 1927, vol. 13, p. 1.
32. J. GRIEVE and J. WHITE : *Journal of the Royal Technical College, Glasgow*, 1940, vol. 4, p. 661.
33. R. GRIVEAU : *Comptes Rendus*, 1918, vol. 166, p. 993.
34. H. E. v. GRONOW : *Zement*, 1936, vol. 25, No. 5, p. 61.
35. H. E. v. GRONOW and H. E. SCHWIETE : *Zeitschrift für anorganische und allgemeine Chemie*, 1933, vol. 216, p. 185.
36. G. GRUBE and R. TRUCKSESS : *Ibid.*, 1931, vol. 203, p. 75.
37. T. P. HALL and H. INSLEY : "Phase Diagrams for Ceramists," 1947 : American Ceramic Society.
38. J. H. HILDEBRAND and E. J. SALSTRÖM : *Journal of the American Chemical Society*, 1932, vol. 54, p. 4257.
39. O. F. HONUS : *Zement*, 1936, vol. 25, p. 33.
40. O. F. HONUS : *Ibid.*, 1935, vol. 24, p. 761.
41. W. JANDER : *Zeitschrift für anorganische und allgemeine Chemie*, 1927, vol. 168, p. 113.
42. W. JANDER and A. KRIEGER : *Ibid.*, 1937, vol. 232, p. 39.
43. W. JANDER and H. SENF : *Ibid.*, 1933, vol. 210, p. 316.
44. A. M. JAY : *Journal of The Iron and Steel Institute*, 1945, vol. 152, p. 15.
45. O. K. JOHANNSEN and T. THORVALDSON : *Journal of the American Chemical Society*, 1934, vol. 56, p. 2327.
46. K. K. KELLEY : *Bulletin of the United States Bureau of Mines*, 1941, No. 434.
47. K. K. KELLEY : *Ibid.*, 1934, No. 371.
48. K. K. KELLEY : *Ibid.*, 1949, No. 476.
49. K. K. KELLEY : *Ibid.*, 1936, No. 393.
50. K. K. KELLEY : *Ibid.*, 1937, No. 406.
51. K. K. KELLEY : *Journal of the American Chemical Society*, 1941, vol. 63, p. 1137.
52. K. K. KELLEY : *Ibid.*, 1943, vol. 65, p. 339.
53. K. K. KELLEY : *Ibid.*, 1941, vol. 63, p. 2750.
54. K. K. KELLEY and C. T. ANDERSON : *Bulletin of the United States Bureau of Mines*, 1935, No. 384.
55. K. K. KELLEY, F. S. BOERICKE, G. E. MOORE, E. H. HUFFMAN, and W. M. BANGERT : *United States Bureau of Mines*, 1944, *Technical Paper* No. 662.
56. K. K. KELLEY, S. S. TODD, and C. H. SHOMATE : *Journal of the American Chemical Society*, 1948, vol. 70, p. 1350.
57. E. G. KING, D. R. TORGESON, and O. A. COOK : *Ibid.*, 1948, vol. 70, p. 2160.
58. E. KLEVER : *Glastechnische Berichte*, 1929, vol. 3, p. 85.
59. K. KÖRBER and W. OELSEN : *Mitteilungen aus dem Kaiser-Wilhelm-Institut fur Eisenforschung*, 1932, vol. 14, p. 181.
60. F. KÖRBER and W. OELSEN : *Ibid.*, 1933, vol. 15, p. 271.
61. F. C. KRACEK : *Journal of the American Chemical Society*, 1930, vol. 52, p. 1436.
62. F. C. KRACEK, G. W. MOREY and H. E. MERWIN : *American Journal of Science*, 1938, vol. 35*A*, p. 143.
63. C. KRÖGER and E. FINGAS : *Zeitschrift für anorganische und allgemeine Chemie*, 1935, vol. 225, p. 1.
64. C. KRÖGER and E. FINGAS : *Ibid.*, 1933, vol. 213, p. 27.
65. LANDOLT-BÖRNSTEIN : *Physikalische-Chemische Tabellen*, 1923, 1550. Vol. 2. H.W.
66. W. LERCH and L. T. BROWNMILLER : *Journal of Research of the National Bureau of Standards*, 1937, vol. 18, pp. 609, 622.
67. G. N. LEWIS : *Journal of the American Chemical Society*, 1906, vol. 28, p. 1380.
68. G. H. B. LOVELL, G. R. RIGBY, and A. T. GREEN : *Transactions of the British Ceramic Society*, 1947, vol. 46, p. 200.
69. G. MALQUORI and V. CIRILLI : *Gazzetta Chimica Italiana*, 1945, vol. 75, p. 137.
70. M. W. MCCREADY : *Journal of Physical and Colloid Chemistry*, 1948, vol. 52, p. 1277.
71. H. J. MCDONALD and H. SELTZ : *Journal of the American Chemical Society*, 1939, vol. 61, p. 2407.
72. H. F. MCMURDIE : *Journal of Research of the National Bureau of Standards*, 1941, vol. 27, p. 499.
73. C. G. MAIER : *Bulletin of the United States Bureau of Mines*, 1942, No. 436.
74. G. MARCHAL : *Journal de Chimie Physique*, 1926, vol. 23, p. 38.
75. C. MATIGNON and M. SÉON : *Comptes Rendus*, 1932, vol. 194, p. 2184.
76. R. W. MILLAR : *Journal of the American Chemical Society*, 1929, vol. 51, p. 215.
77. M. A. MOSESMAN and K. S. PITZER : *Ibid.*, 1941, vol. 63, p. 2348.
78. O. MULERT : *Zeitschrift für anorganische und allgemeine Chemie*, 1912, vol. 75, p. 198.
79. O. MULERT : *Ibid.*, 1912, vol. 75, p. 238.
80. B. F. NAYLOR : *Journal of the American Chemical Society*, 1945, vol. 67, p. 2120.
81. B. F. NAYLOR : *Ibid.*, 1946, vol. 68, p. 1077.
82. B. F. NAYLOR : *Industrial and Engineering Chemistry*, 1944, vol. 36, p. 933.
83. B. F. NAYLOR : *Journal of the American Chemical Society*, 1945, vol. 67, p. 466.
84. B. F. NAYLOR and O. A. COOK : *Journal of the American Chemical Society*, 1946, vol. 68, p. 1003.
85. F. NEUMANN : *Zeitschrift für anorganische und allgemeine Chemie*, 1925, vol. 145, p. 193.
86. L. PAULING : " The Nature of the Chemical Bond," 1940, Cornell University Press.
87. L. M. PIDGEON and J. A. KING : *Discussions of the Faraday Society*, 1948, vol. 4, p. 197.
88. G. A. RANKIN and F. E. WRIGHT : *American Journal of Science*, 4th Series, 1915, vol. 39, p. 5.
89. E. RENGADE ; *Comptes Rendus*, 1907, vol. 145, p. 236.
90. M. REY : *Discussions of the Faraday Society*, 1948, vol. 4, p. 257.
91. T. W. RICHARDS, A. W. ROWE, and L. L. BURGESS : *Journal of the American Chemical Society*, 1910, vol. 32, p. 1176.
92. F. D. RICHARDSON and J. H. E. JEFFES : *Journal of The Iron and Steel Institute*, 1949, vol. 163, p. 152.
93. F. D. RICHARDSON : *Discussions of the Faraday Society*, 1948, vol. 4, p. 244.
94. F. D. RICHARDSON and J. H. E. JEFFES : *Journal of The Iron and Steel Institute*, 1948, vol. 160, p. 261.

Continued on p. 245

Experiments on Gaseous Mixing in Open-Hearth Furnace Models

By R. D. Collins, B.Sc., and J. D. Tyler

FOREWORD

In Part I* the authors examined the effect on mixing of the size and position of air and gas ports in Maerz-type furnaces. The simplicity of this type of furnace makes it particularly suitable for the study of control by positioning of the ports; the gas port does not project through the end wall, and the only variables in its design are its shape, area, position, and slope. Moreover, there is no knuckle in the roof of the furnace and no contraction of the side walls. Most furnaces in use, however, are not the Maerz type. The semi-Venturi and similar designs have a throat formed by the knuckle of the roof and a simultaneous constriction of the side walls, either or both of which features may be found, in varying degrees, in different furnaces. The gas port is brought into the furnace chamber as an arched block which, if not water-cooled, may vary considerably in length, even in a single furnace, as the block burns back during a campaign. In the present paper the technique used in Part I is applied to a series of modified semi-Venturi designs.

Part II—SEMI-VENTURI DESIGNS

SYNOPSIS

The technique of using models to determine the degree of mixing, described in Part I (Maerz design), is applied to a series of modified semi-Venturi designs. The most significant factors are (*a*) size of gas port (multiple ports provide very quick mixing without increased uptake pressures), (*b*) slope of gas port, (*c*) length of gas port, (*d*) distance of throat from gas port, and (*e*) sharpness of throat and knuckle contraction. These affect not only the degree of mixing but also the shape of the mixing pattern. Thus, the slope of the gas port controls stratification, multiple gas ports give high initial rate of mixing, and throat modifications affect the later stages of mixing.

A provisional theory of mixing is developed in which two zones are considered separately, the space occupied by the jet of gas issuing from the gas port, and the remainder of the furnace space. The experimental results are explained on this principle.

Introduction

THERE are many factors to be considered in the design of an actual furnace, some of which (as, for example, flame luminosity) call for a particular scheme of mixing, while others, for example refractory life, must sometimes be given priority over good mixing. If mixing is completed too quickly the flame becomes non-luminous and heat transfer suffers, whereas if it is too slow some of the calorific value of the fuel is wasted. Possibly the ideal is rapid partial combustion to produce a hot flame, followed by a slow completion of mixing, to burn out the luminosity-producing particles at the far end of the furnace. Again, since refining is an oxidation process, high gas concentrations at the hearth level are not an advantage, but since the erosion of silica brick is accelerated by a reducing atmosphere, stratification may be necessary to protect the roof. These experiments are intended to classify the effects of possible structural alterations to a furnace, to determine how best to obtain a desired distribution of mixing concentrations.

A provisional theory of mixing is proposed which accounts qualitatively for the effects observed in the experiments. In a series of experiments carried out by Rummel,[1] gas and air emerged from what was, in effect, one rectangular duct separated into two halves by a partition. Thus, although the gas and air entered quite unmixed they formed a single jet, there being no discontinuity of velocity between them, and mixing was controlled by the flow within the jet. Rummel investigated the effect on mixing of the shape of the box. In successive experiments the height was altered, the dead corners filled in, and the jet made to flow through an orifice (*see* Fig. 1). In each experiment no significant change appeared, provided that nothing projected into the volume normally occupied by the jet. This result is important, because the flow outside the jet must obviously have been considerably altered.

In interpreting the results of our experiments the principle has been adopted of considering the flow

**Journal of The Iron and Steel Institute*, 1949, vol. 162, Aug., p. 457.

Paper SM/A/182/48 of the Steel Practice Committee of the Steelmaking Division of the British Iron and Steel Research Association, received 28th March, 1950. The views expressed are the authors' and are not necessarily endorsed by the Committee as a body.

Mr. Collins and Miss Tyler are in the Aerodynamics Section of the Physics Department of the Research Association.

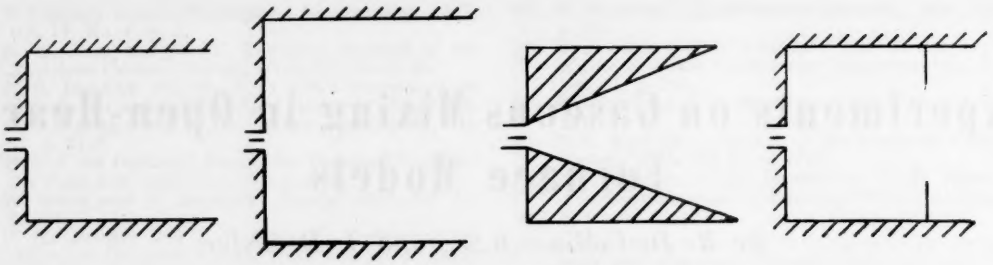


Fig. 1—Rummel's experiment

system in two parts ; firstly the jet itself, and secondly the remainder of the chamber. As air velocities outside the jet are small compared with those inside, it is expected that the rate at which the fluid is drawn into the jet and is mixed with it will be dependent on two factors only, the dimensions of the port from which it emerges, and the position and shape of any surface against which it strikes. Since practical considerations prevent any wall being covered by the flame, the only variables governing this second factor are the angle of the port and the distance from the port at which the jet strikes the hearth.

The knuckle and throat will not, by this theory, affect the amount of fluid entrained by the jet, or the way in which this mixes with the fluid already there, but it may profoundly influence the flow outside it. If this then results in a change of concentration in the region immediately surrounding the jet from which the entrained fluid is drawn, then the downstream concentrations in the jet will also be altered, because, although the same quantity of fluid is drawn in, the amount of air is different.

EXPERIMENTAL PROCEDURE

The models used were $\frac{1}{15}$-scale, under conditions adjusted for Reynolds similarity. Geometrical similarity was preserved as far as the middle of the furnace; beyond this the flow continued through a rectangular box. The original design was that of the *S* furnace at the Templeborough Melting Shop of Messrs. Steel, Peech, and Tozer,[2] the layout of the apparatus being the same as in Part I of this paper.

Concentrations were measured, as percentage gas from the gas port, by means of an infra-red gas analyser, these measurements being made across furnace sections corresponding to distances* of 8 ft. 3 in., 10 ft. 10 in., 13 ft. 9 in., and 18 ft. 10 in., from the end wall. The normal length of the block, from the end wall to the front face half-way up the port, was 3 ft. 3 in., so that the ' flame ' had travelled 5 ft., 7 ft. 7 in., 10 ft. 6 in., and 15 ft. 7 in. at each section respectively. The first of these sections was at the narrowest part of the throat, and the third was at the end of the expansion following it. A fourth section was necessary because of the slow mixing of some of the models.

The length of the original furnace from end wall to end wall was 56 ft. 2 in., so that, allowing for the greater length of the *S* furnace, the third section corresponds approximately to the third section in Part I. Figure 2*a* gives the concentration pattern in this model, using an air/gas ratio of 1·5 : 1, the unmodified throat being 11 ft. wide and 4 ft. 6 in. high. Figure 2*b* shows the negligible effect of halving the flow rate while maintaining the air/gas ratio constant. In Fig. 3*a* the air/gas ratio is reduced to 1 : 1 by reducing the supply of air. Figure 4 shows the effect of halving the area of the top of the air uptakes, thus doubling the air velocity and quadrupling the dynamic head in the uptakes. (The fourth section had not been introduced when this experiment was made.)

In Fig. 5 the original gas port, cut in a large block, has been replaced by a semi-circular arch of uniform thickness (7 in.) of the same length, shape, area, and slope. The port was made in sections, for use in later experiments. In Figs. 6*a–c*, models differing only in ramp slope and the height of the roof at the top of the ramp were used. The slopes of models A, B, C, and D were 46°, 31°, 24°, and 9° respectively ; central elevations are indicated in Fig. 7.

In Figs. 8*a–c*, gas ports 26 in. longer and 13 in. and 30 in. shorter, respectively, than the original were used. As the patterns were similar for each gas port, a longitudinal section was studied in detail, readings being taken at intervals of 15 in. (Fig. 9).

There are two possible ways of lowering the knuckle ; the roof ramp, which slopes down from above the uptakes, may be lowered bodily, also requiring a lowering of the end roof above the uptakes, or its slope may be increased to cover the increased difference in level between its ends. But as Fig. 6 shows that for a given knuckle height the mixing is independent of roof ramp slope (provided the end roof is not too low), it is only necessary to make one series of tests of knuckle height.

Figures 10*a* and *b* show for two port lengths the effect of lowering the knuckle 15 in., and of narrowing the throat by bringing each side wall in 15 in. Further lowering the roof would bring it into the region corresponding to the flame, but the throat area was reduced again by moving the side walls another 15 in. (Figs. 10*c* and *d*). Instead of increasing the sharpness with which the side walls converge, they were next extended to form a new throat 30 in. farther from the block end (Fig. 11). The walls were brought in 25 in. and the knuckle down 15 in., so that the throat area was nearly the same as in Figs 10*c* and *d*. With this arrangement the short port was used.

The slope of the gas port was altered by building the gas-port arch on to a wedge-shaped platform. In Fig. 12*a* the original gas port was used with an

* All measurements refer to full scale, not model dimensions.

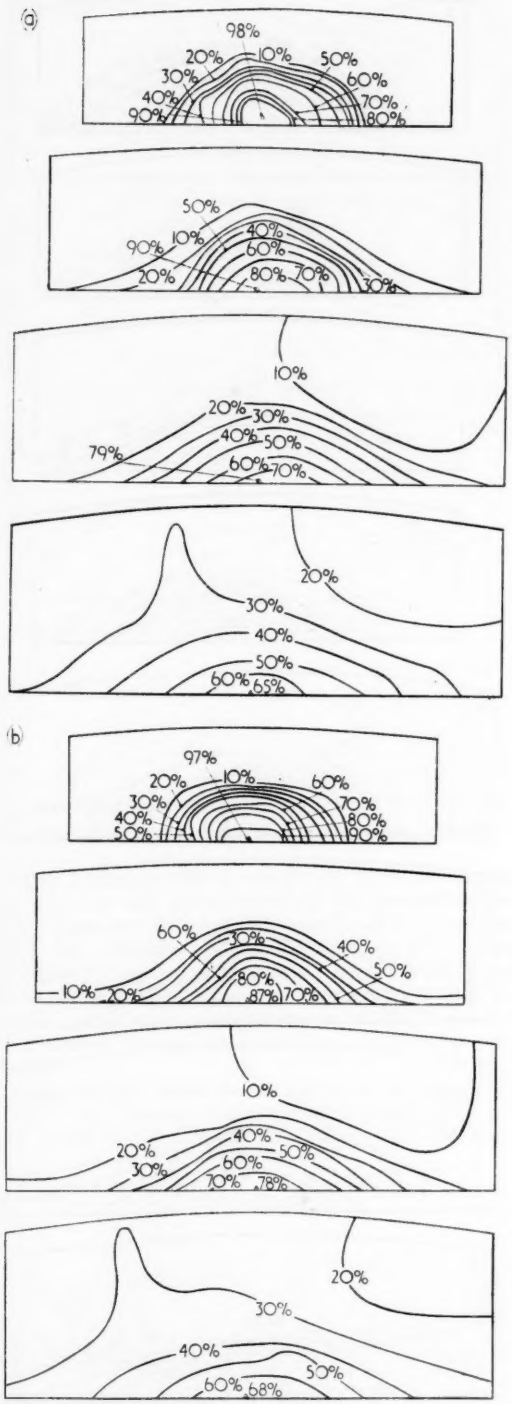


Fig. 2—Mixing contours across four successive sections of unmodified furnace model. (*a*) Air/gas ratio 1·5 : 1, (*b*) flow rate halved, air/gas ratio maintained

unmodified (*i.e.* as Fig. 5) throat, and the gas-port slope was reduced from 1 in 6 to 1 in 17. Figures 12*b* and *c* show the effects of shortening the gas port and lengthening the mixing region before the throat, respectively. The last model used was similar to the original design in all respects except the gas port; no block was used, but three equal circular ports were cut in the end wall, the total area being made the same as that of the original. They did not project into the furnace but formed a row of 15-in. dia. holes along the end wall, spaced at a distance of 30 in. between centres, at the level of the original gas port: their slope was 1 in 12. Mixing was so good by the third section (Fig. 13) that no fourth section was taken.

RESULTS

Factors of Small Significance

Figure 2*a* (original model) clearly shows pronounced horizontal stratification, incomplete mixing even beyond the first door (section 4), and asymmetrical distribution of concentration beyond the throat in

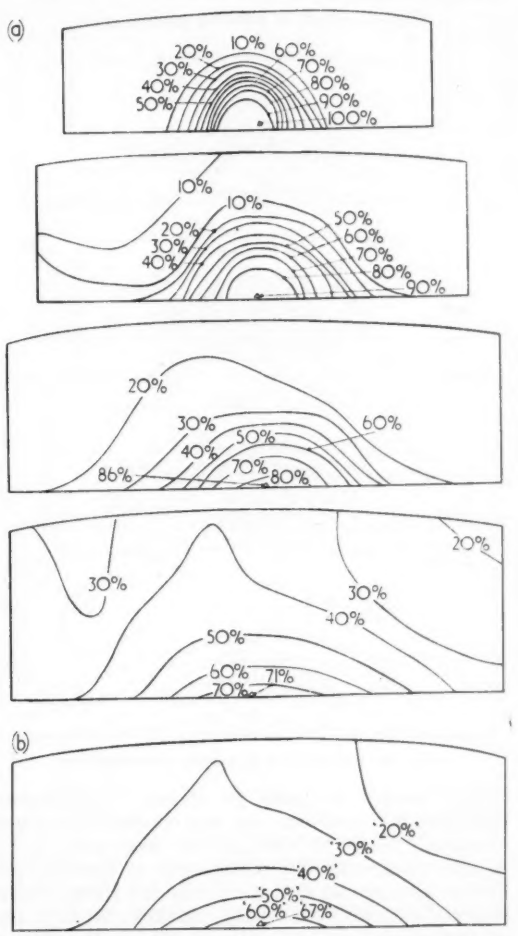


Fig. 3—(*a*) As Fig. 2, but with air/gas ratio reduced to 1 : 1. (*b*) Prediction, by calculation, of effect of increasing air/gas ratio to 1·5 : 1. Based on experimental results of Fig. 3*a*, to compare with Fig. 2*a*

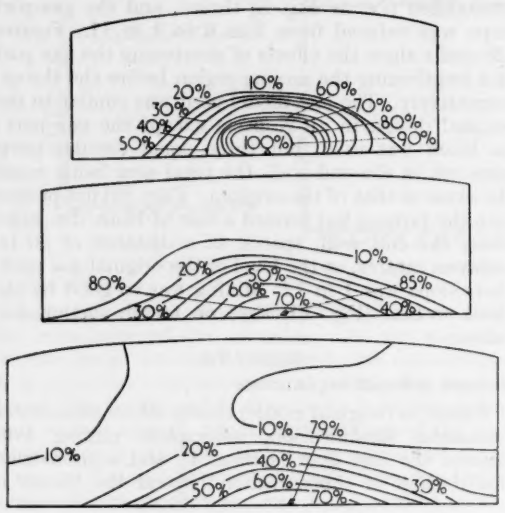


Fig. 4—Effect of halving uptake area

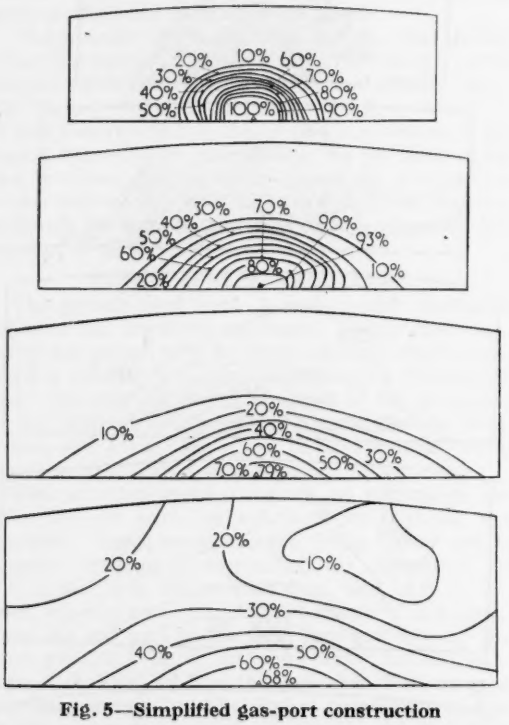


Fig. 5—Simplified gas-port construction

regions outside the main jet of gas. The inference that back flow occurred here was checked by a simple visualization test in which sparks were used, and is in agreement with the experiments of Halliday and Philip[3] on a similar design. Unlike the Maerz designs (especially those with central uptakes), all high concentration contours end on the hearth and there are no closed curves. The ingoing end of the hearth is occupied mainly by excess gas, in spite of the 50% excess air supplied.

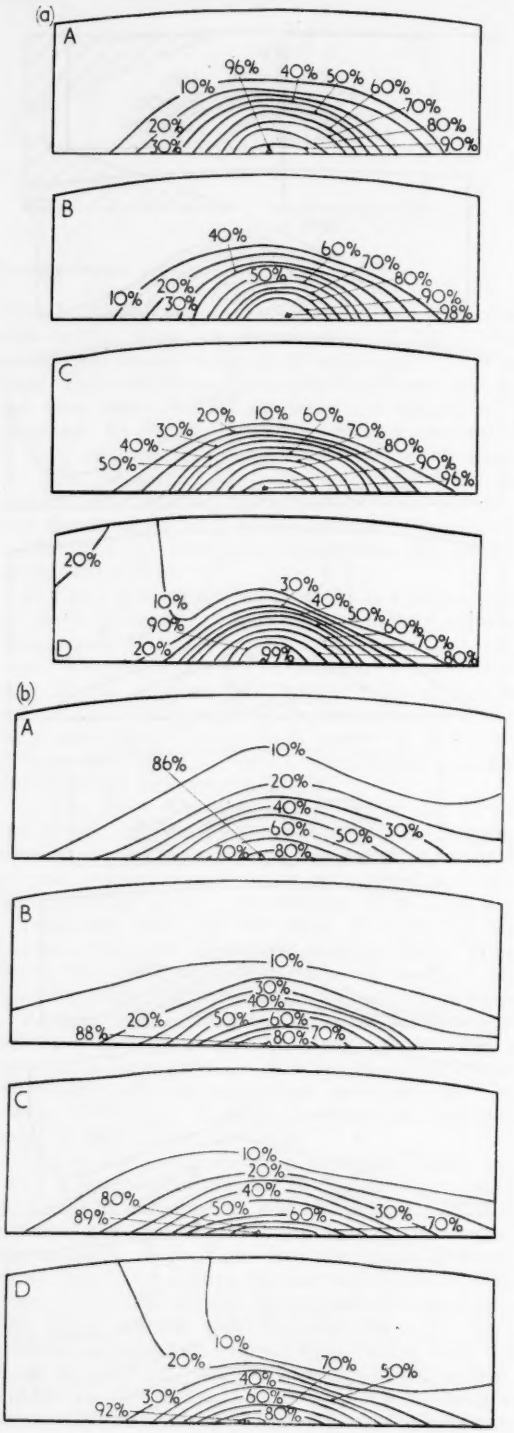


Fig. 6*a*, *b*—Effect of ramp roof slope: (*a*) on 2nd section, (*b*) on 3rd section

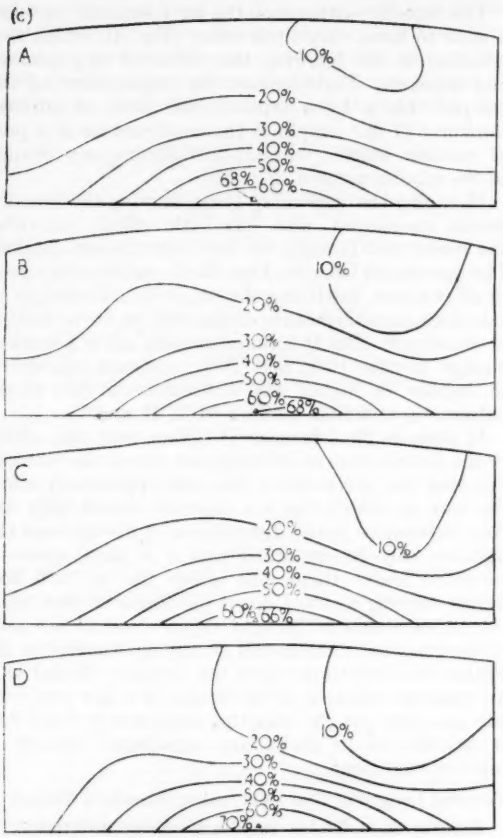


Fig. 6c—Effect of ramp roof slope on 4th section

A 2 : 1 change of flow rate has no effect on mixing (*cf.* Figs. 2*a* and *b*), so that it is unnecessary to use more than one flow rate for each model; therefore Reynolds criterion is also not critical, since it can be satisfied by choice of flow rate. Similarly, if it can be shown that the changes produced by varying the air/gas ratio follow a simple universal law, it will not be necessary to test this operating condition for each design.

Suppose that when the air/gas ratio is changed to n times its previous value the ratio of air to gas at any point in the furnace also changes in the same

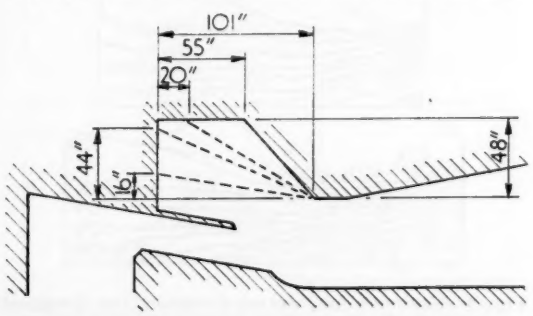


Fig. 7—Central elevations of ramp roof models

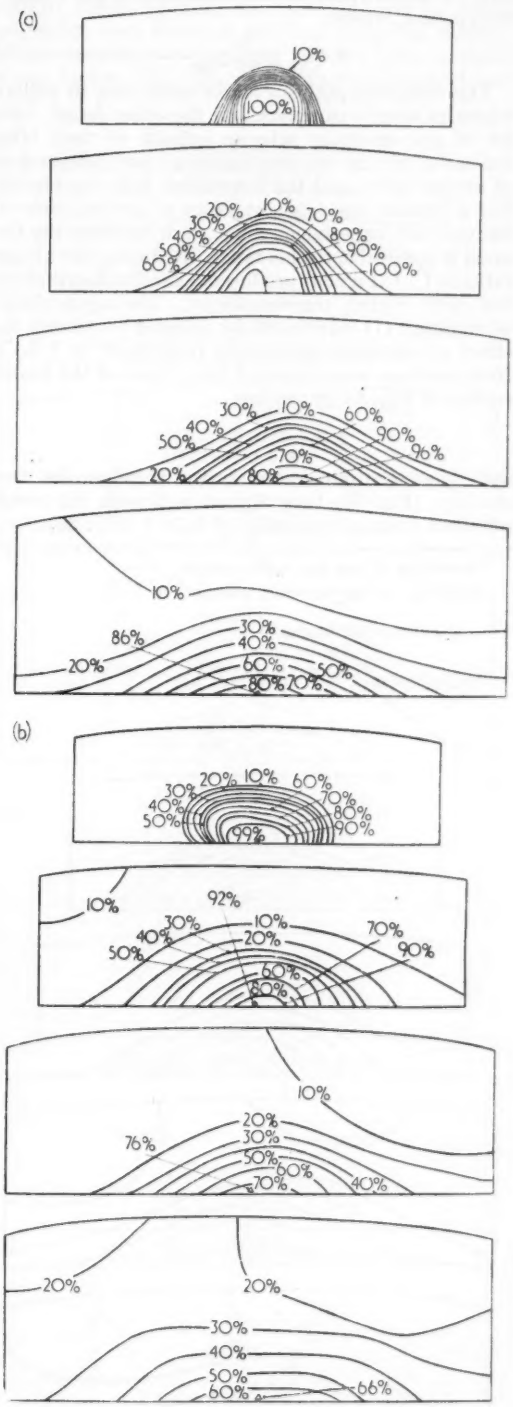


Fig. 8*a*, *b*—Effect of gas-port length (based on the length of the original port). (*a*) Increased 26 in., (*b*) decreased 13 in.

ratio ; it follows that the concentration of gas changes from c_o to c, where

$$c = \frac{c_o}{c_o + n(1-c_o)} \quad \ldots\ldots(1)^*$$

This simple hypothesis is obviously true in regions where mixing is complete ; on the other hand, for a jet of gas emerging into an infinite or very large volume of air the jet concentrations are independent of air/gas ratio, and the hypothesis fails completely. For a furnace the relevant range of air/gas ratios is limited, and experiment must show whether the formula is applicable to this range. Reducing the air/gas ratio to 1 : 1 (Fig. 3*a*) produced a similar distribution, but with higher concentrations. The applicability of equation (1) was tested by using it to predict the effect of changing the air/gas ratio back to 1·5 : 1. New readings were obtained from those of the fourth section of Fig. 3*a* by putting

$$c = \frac{c_o}{c_o + 1{\cdot}5(1-c_o)},$$

and when contours were drawn through the new readings (Fig. 3*b*) they agreed well with the result obtained at an air/gas ratio of 1·5 : 1 (Fig. 2*a*).

* Quantity of gas per unit volume $= c$
Quantity of air per unit volume $= 1-c$

$$\therefore \text{ ratio of air to gas} = \frac{1-c}{c}$$

$$\text{By hypothesis, } \frac{1-c}{c} = n\left(\frac{1-c_o}{c_o}\right),$$

$$\therefore\ c = \frac{c_o}{c_o + n(1-c_o)}$$

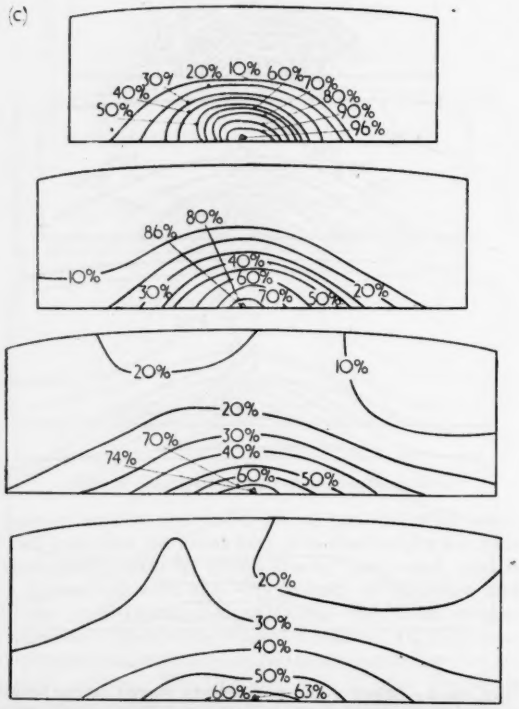


Fig. 8c—Gas-port length decreased 30 in.

The velocity with which the air leaves the uptakes is seen to have very little effect (Fig. 4), which is a justification for ignoring the effect of slag pockets and checkers. Furthermore, the replacement of the gas-port block by a semi-circular arch of uniform thickness (7 in.) simplifies the construction of a port of variable length, without introducing any change to the mixing pattern (Fig. 5).

Changing the roof ramp slope, leaving the knuckle height unchanged, also has little effect, provided the roof is not brought too low over the air uptakes. The agreement between Figs. 6*a*, *b*, and *c* is very good in all sections, justifying the use of knuckle height as the characteristic feature of the roof, so far as mixing is concerned. The D furnace sections show a marked change in the 10% and 20% contours ; however, in regions of higher gas concentration this model behaves in a similar manner to A, B, and C.

It appears that furnace D differs from the others in the distribution of incoming air across the furnace, but that this disturbance does not appreciably affect the rate at which the gas becomes mixed with air. Any differences in the distribution of air between the uptakes can be smoothed out if a large space is provided above them into which the air will flow before moving forward down the furnace. But when the furnace roof is brought down close to the arch of the gas port, as in model D, any asymmetry in the uptake flow continues into the furnace. Model D is an extreme example of the design of a low roof over the gas port, yet the resulting asymmetry of air flow is insufficient to make any significant change in mixing conditions.

Varying Length of Gas Port, using Standard Throat

Figures 8*a–c* are the results for three different port lengths (*cf.* Fig. 5). There is a progressive improve-

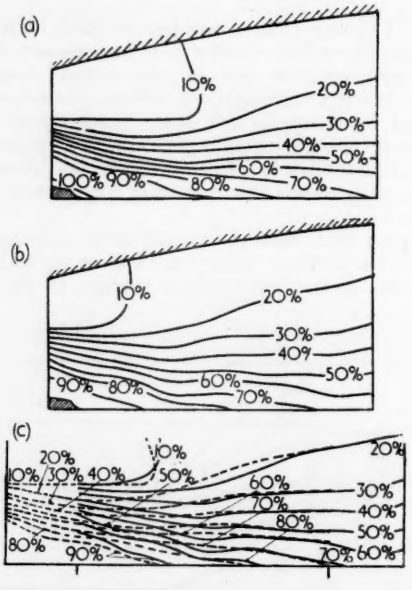


Fig. 9—Contours for central elevation. (*a*) Original port, (*b*) shortest port, (*c*) superposition of (*a*) on (*b*), with 27-in. horizontal shift

ment as the gas port is shortened, which may be because mixing starts farther back each time. The somewhat greater difference between Fig. 8*a* and the other results occurs because of the large change of port length, and the closeness of the port to the positions of measurement; the changes in mixing pattern occurring near the port are always more noticeable than those in the final stages of mixing, as may be seen by comparing the first three sections of any design. The difference between sections 1 and

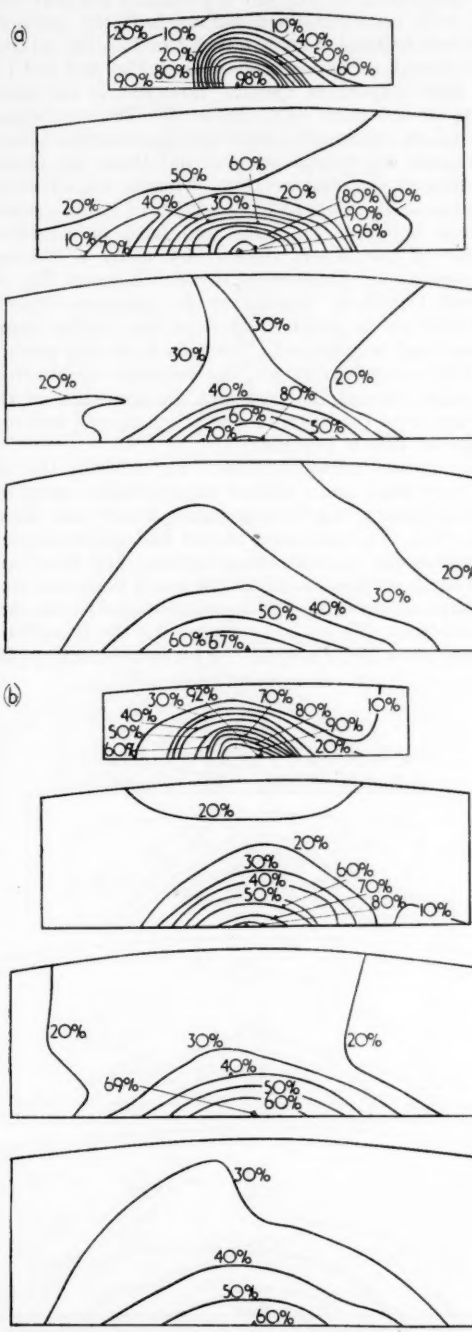


Fig. 10*a*, *b*—Effect of throat modifications. Knuckle lowered 15 in., side walls brought in 15 in. (*a*) Original gas port, (*b*) short gas port

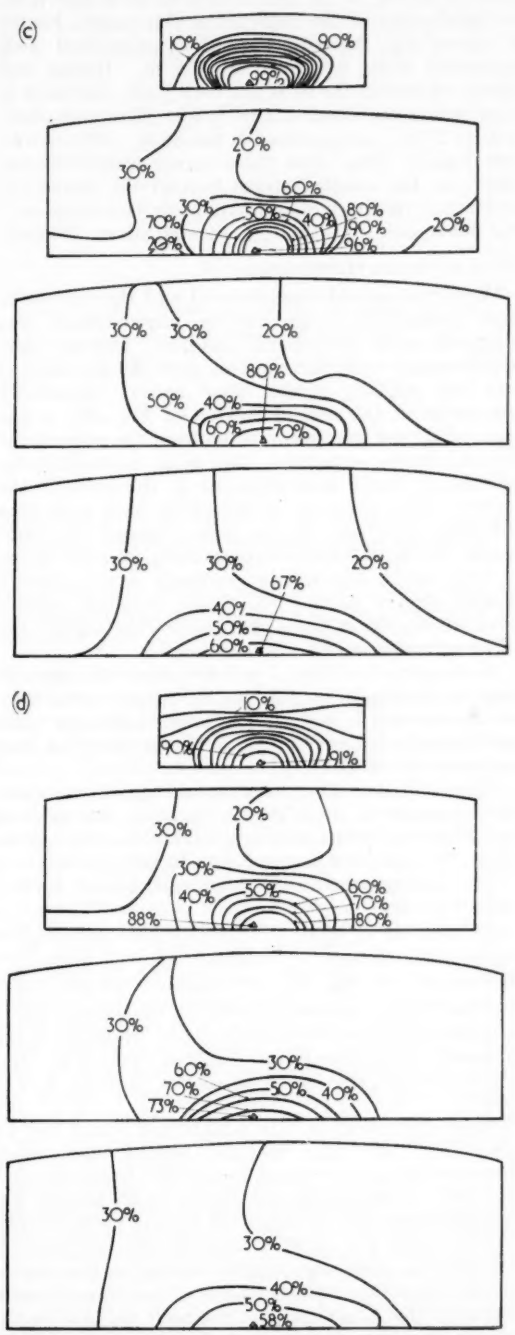


Fig. 10*c*, *d*—Effect of throat modifications. Knuckle lowered 15 in., side walls brought in 30 in. (*c*) Original gas port, (*d*) short gas port

2 is always greater than that between sections 2 and 3.

Figures 9*a* and *b* are the concentration patterns for the original port length and the shortest port (30 in. shorter) respectively, along the centre line of the furnace. It was difficult to assess a slight improvement in mixing at the fourth section, as is shown by the small slope of the contours at this point. Figure 9*c* shows Fig. 9*a* with Fig. 9*b* superimposed with horizontal shift, to give the best fit. During the throat expansion the fit is not very good, but there is good agreement beyond this point. The horizontal shift is 27 in., compared with the 30-in. difference in port length. Thus with these throat conditions the effect, on the concentrations beyond the throat, of shortening the port is approximately the same as if the flame were pushed back an equivalent distance.

Effect of Throat Modifications

When the knuckle was lowered and the side walls were contracted, a progressive improvement was observed with decreasing gas-port length; the improvement with the shortest port (30 in. shorter) was only slightly greater than before. Especially noticeable in the second section of Fig. 10*a* is the layer of almost pure air, coming from the edge of the throat, which separates the high concentrations around the flame from stale air at the sides of the furnace. This stale air is caused by back flow from the sides and roof. In the latter, almost stagnant, region there is remarkably uniform concentration, in contrast to the steady gradients in the directly flowing regions of the jet. Since, with the shorter port, most mixing takes place before the throat, the effect of throat modifications is small.

A comparison of Figs. 5 and 10*a* shows an improvement in mixing, in addition to the change in the form of the pattern. This improvement, although quite noticeable, is not large and is somewhat less than that produced by shortening the port.

With a further 15-in. contraction of the side walls, there is again a small improvement in mixing, and the difference between the original and the short ports (Figs. 10*c* and *d* respectively) is slightly greater.

The highest reading (%) of each fourth section is as follows :

	Original (standard)	15 in. on roof 15 in. at sides	15 in. on roof 30 in. at sides
Original port	68 (Fig. 5)	67 (Fig. 10*a*)	67 (Fig. 10*c*)
Short port	63 (Fig. 8*c*)	60 (Fig. 10*b*)	58 (Fig. 10*d*)

These figures indicate that throat dimensions are of greater importance for a short port, when the flame is nearly filling the throat (Fig. 10*d*, section 1). But mixing is still slow even when the shortest port is used.

Low concentrations are maintained round the jet (Fig. 10*d*) for some distance beyond the throat, because the narrow throat forces the air sharply into the gas. Lengthening the throat gives similar low concentration and a degree of mixing in the fourth section (Fig. 11) equal to that in the very narrow throat (Fig. 10*d*), the highest reading in the section again being 58%. But the layer of low concentration between the flame and the stagnant regions by the wall (Fig. 10*d*, section 2) has gone, and the flow pattern resembles Fig. 10*b*, which represents a throat of very similar dimensions.

Gas-Port Slope

In the modifications considered so far, even the combination of the shortest port and the best throat gave only a limited improvement. But by changing the slope of the gas port a considerable effect was at once produced. In Fig. 12*a* the original gas port was used with an unmodified throat, and the gas-port slope was reduced from 1 in 6 to 1 in 17. The mixing at the fourth section is as good as in Figs 10*d* and 11. The most important feature, however, is the similarity, in the early sections, to the Maerz designs. The highest concentrations do not appear at the hearth level until the fourth section, and there are closed contours in the first section. Thus a semi-Venturi furnace can be made to have a layer of lower concentrations between the flame and bath (a condition typical of the Maerz design) by using a reduced gas-port slope. Conversely it was shown in Fig. 4*c* of Part I that by increasing the gas-port slope a stratification as great as that in the typical semi-Venturi can be produced. The main factors in producing high stratification are the exclusion of air from the under side of the port and the spreading of the jet itself over the hearth. The effect of wall and roof on the air flow is secondary.

Mixing was again improved (Fig. 12*b*) by the use of a short port, and a further improvement was given by lengthening the mixing region before the throat (Fig. 12*c*). The extended throat had greatest effect on maximum concentration between the third and the fourth sections, whereas the small slope was most effective in lowering the concentrations in the first two sections. This is to be expected if the importance of the throat lies in keeping the jet surrounded by pure

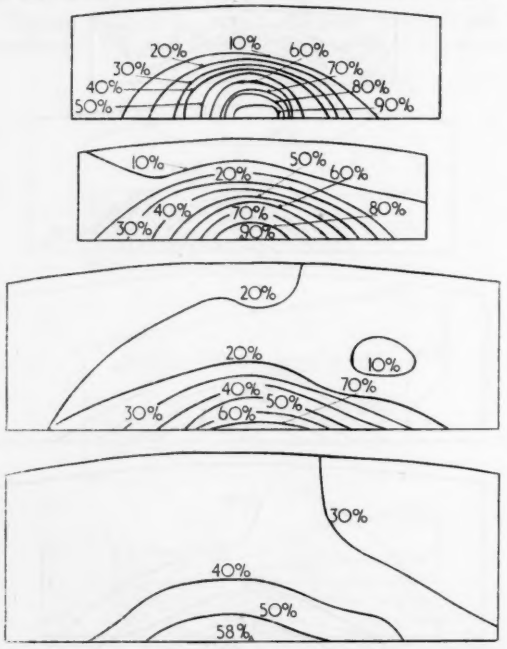


Fig. 11—Short gas port and lengthened throat. Side walls converge to throat 30 in. farther from block end. Width of throat 25 in. less and height 15 in. less than in original model

air for as long as possible, since this air will only reach the centre of the jet some distance downstream from

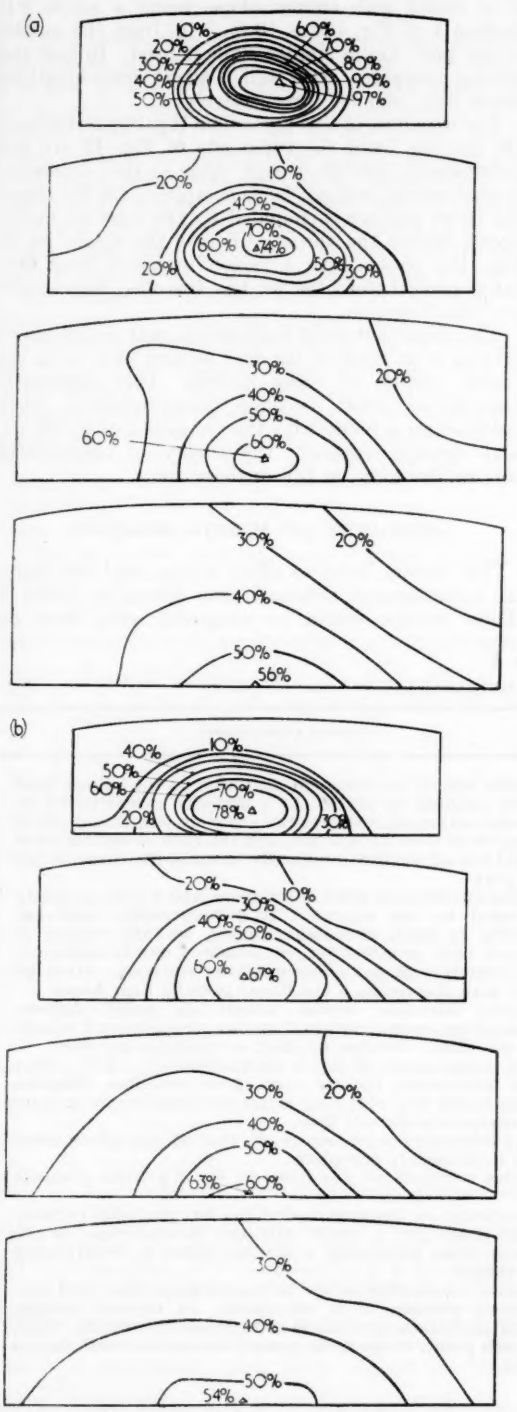


Fig. 12*a*, *b*—Gas-port slope reduced from 1 in 6 to 1 in 17; unmodified throat. (*a*) Original gas port, (*b*) short gas port

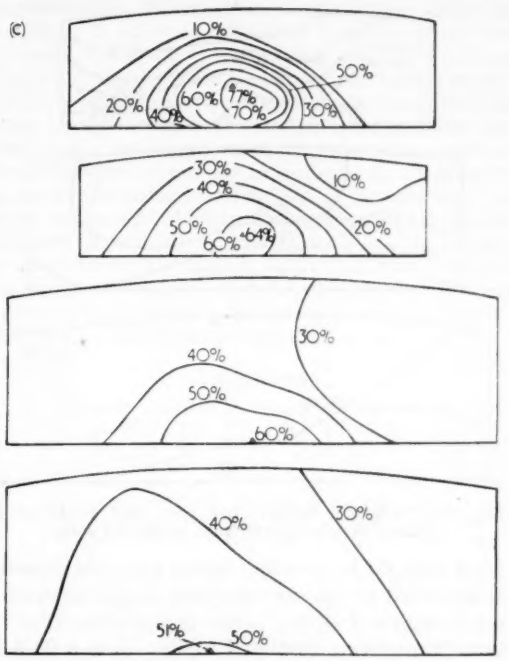


Fig. 12c—As Fig. 12b, but with lengthened throat

the throat. On the other hand, the small slope reduces the screening effect of the floor and enables air to be entrained from the lower part of the jet.

Multiple Gas-Port Model

In the last two tests, mixing was better than that of the original Maerz design of Part I but was not as good as in the single air-uptake modification of the Maerz. Using a model of the original design, but with the gas port replaced by three equal circular ports in the end wall, gave a great improvement in mixing (Fig. 13), which was so good by the third section that no fourth section was necessary.

Next to the extremely good mixing, the most important feature of these sections is that stratification is preserved : there is a layer of air along the roof which does not completely disappear even when mixing is nearly complete. The last section shows concentrations increasing from roof to hearth ; they also increase from front to back wall and this may be attributed to greater back flow at this side. The same effect occurs to a greater or lesser extent in all the models tested. The greater back flow on the back-wall side is shown in the photographs of flow in the water model of the same furnace studied by Halliday and Philip.[3]

When mixing in a free jet, the length in which a given amount of air is entrained into the jet is proportional to the diameter of the jet.* If the area of a

* If L is the distance in which a given degree of mixing takes place in a free jet of diameter d, then $L/d = f(R)$, where R is the Reynolds number. This expression is found, experimentally, to change only slowly with R. if R is large. If the mean velocity at the source is constant, R varies with d and, for reasonable changes, L is approximately proportional to d.

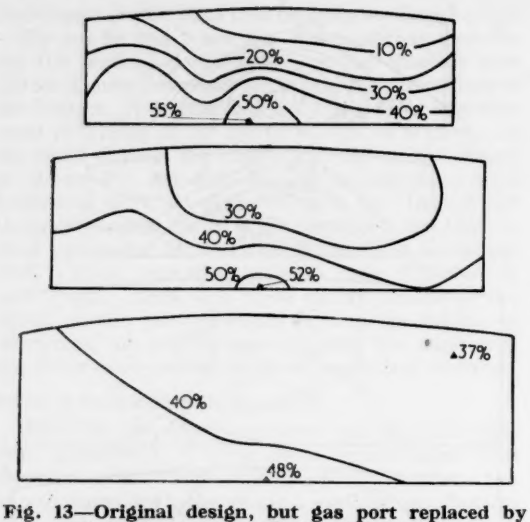


Fig. 13—Original design, but gas port replaced by three circular ports flush with end wall

jet is reduced to $\frac{1}{3}$ of its original area, the diameter is decreased to $\frac{1}{\sqrt{3}}$, and hence the length in which a given degree of mixing occurs is also reduced in the same proportion. Section 1 of Fig. 13 is 8 ft. 3 in. from the mouth of the port; if the free jet result were applicable, the mixing here would correspond to a section $\sqrt{3}$ times as far (14 ft. 4 in.) from the port of a model with similar slope, using a single jet. Section 4 of Fig. 12*a* is 15 ft. 7 in. from the mouth of the port, and a similar slope is used. In fact the mixing compares very well, highest concentrations being 55% and 56% respectively.

The closeness of this agreement is partly fortuitous. On the one hand the three jets of Fig. 13 are not independent but affect each other as they intermix, so that mixing will not be as complete. On the other, the three jets are surrounded by the pure air in the region before the throat, whereas the single jet of Fig. 12*a* passes into a region in which back flow takes place before the jet has travelled half-way to the fourth section.

The important point is, however, that in this model mixing is as good in the first section as it is in the fourth section of other models. This apparently remarkable result becomes understandable when comparison is made with the behaviour of a free jet, and strongly supports the theory of open-hearth mixing discussed in the introduction.

SUMMARY OF MIXING RESULTS

The factors found to affect mixing, and the degree of improvement obtained, are given in Table I. These results should be compared with those for

Table I

TABULATED SUMMARY

Modification	Degree of Improvement	Cause of Improvement
Multiple gas ports	Very large	Increases rate of entrainment, initially, as the square root of the number of ports. At a distance proportional to the separation of the ports the separate jets would begin to interfere with each other, and the rate of entrainment would fall off until it eventually became the same as for one port
Air port brought under gas port (*see* Part I)	Very large	Provides air to lower sides of jet, from which it is normally excluded by the hearth. If a moderately high air velocity is used, turbulent mixing at this surface is greater than in a free jet, recirculated gas is excluded, and hearth-level gas concentrations reduced. Must be used with discretion if the flame is to be kept down
Reduced size of gas port (*see* Part I)	Large	Decreases distance across which air must diffuse. Limited by consideration of uptake pressure and waste-gas partition. Similar in effect to multiple gas port
Slope of gas port reduced	Large	Allows some access of air to underside of jet. Less effect than positioning the air port, since turbulent diffusion at the under side of the jet is not increased by the impact of a perpendicular air flow
Shortened gas port	Moderate	Causes mixing to start sooner, so that by any given point it is more nearly complete
Throat extended towards bath	Moderate	Excludes recirculated gas from jet for a greater distance
Throat made sharper by bringing the walls in and the knuckle down	Moderate	By throwing air inwards round the jet, excludes recirculated gases for a short distance downstream of the throat, thus producing a similar effect to lengthening the throat
Increasing air/gas ratio	Moderate	Increases proportion of air in recirculated gas, and also reduces amount of it entrained. In normal design, effect at distant sections is to increase the air/gas ratio, at each point, in the same proportion as the total air/gas ratio.
Structural changes in outer brickwork of gas port	No significant change	
Absolute flow rate		

heat transfer in similar conditions produced in the Shelton experimental open-hearth furnace.[4]

CONCLUSIONS

These results show good qualitative agreement with the theory, discussed in the introduction, by which the flow system was divided into a high-energy jet of gas and a surrounding region of slower flow. The rate of entrainment into this jet and mixing within it are regarded as dependent only on the gas port and its position relative to the hearth. Modifications to throat and knuckle, however, modify the surrounding flow and, by controlling the concentrations in the region from which gases are entrained into the jet, have a limited effect on the concentrations within it.

Shortening the gas-port length had the effect of moving the jet backwards without much alteration of its mixing pattern. Subdivision of the jet produced an extremely powerful effect, of the same order as is found in a free jet. Other than this, the greatest change is produced by altering the angle at which the jet strikes the bath ; increasing the angle makes the jet spread over the floor and excludes air from reaching the under side. It was shown in Part I that the deliberate provision of air to this surface counteracted the effect and greatly improved mixing.

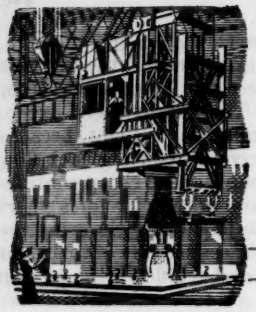
Changes to the wall and roof produced a slight improvement. When these changes were effective, a change in the concentrations around the jet was present ; moreover, the effect was downstream from the point of modification. The improvement expected from altering throat dimensions is slight, because even a wide throat is effective in reducing back flow past it to a very small amount, and a sharp contraction will only project air around the jet for a short distance. By using multiple jets, or by throwing the air at the gas jet (which increases the rate of turbulent diffusion as well as excluding back flow), the jet can be made to entrain enough air for combustion before the throat is reached. With a large jet, on the other hand, there is a limit to the rate of mixing, no matter how well recirculation is excluded.

References

1. K. RUMMEL : *Archiv für das Eisenhüttenwesen*, 1937, vol. 10, May, pp. 505–510 ; June, pp. 541–548 : vol. 11, July, pp. 19–30 ; Aug., pp. 67–80 ; Sept., pp. 113–123 ; Oct., pp. 163–181 ; Nov., pp. 215–224.
2. J. H. CHESTERS and M. W. THRING : *The Iron and Steel Institute*, 1946, *Special Report No.* 37.
3. I. M. D. HALLIDAY and A. R. PHILIP : *Journal of The Iron and Steel Institute*, 1949, vol. 162, Aug., p. 401.
4. A. H. LECKIE, J. R. HALL, C. CARTLIDGE, J. F. ALLEN, J. H. COOK, and G. FENTON : *Ibid.*, 1947, vol. 155, p. 392 ; 1948, vol. 160, p. 37.

THERMODYNAMICS OF COMPOUNDS BETWEEN OXIDES—Continued from p. 234

95. H. RICHTER : *Zement*, 1942, vol. 31, p. 505.
96. W. A. ROTH and W. BERTRAM : *Zeitschrift für Elektrochemie*, 1929, vol. 35, p. 297.
97. W. A. ROTH and P. CHALL : *Ibid.*, 1928, vol. 34, p. 185.
98. W. A. ROTH and F. MÜLLER : *Zeitschrift für physikälische Chemie*, 1929, vol. 144, p. 257.
99. W. A. ROTH and H. TROITZSCH : *Archiv für das Eisenhüttenwesen*, 1932, vol. 6, p. 79.
100. W. A. ROTH and F. WIENERT : *Ibid.*, 1934, vol. 8, p. 457.
101. W. A. ROTH and U. WOLF : *Zeitschrift für Elektrochemie*, 1940, vol. 46, p. 232.
102. T. G. SAHAMA and D. R. TORGESON : *United States Bureau of Mines*, 1949, *Report No.* 4408.
103. R. SCHENCK, H. FRANZ, and A. LAYMANN : *Zeitschrift für anorganische und allgemeine Chemie*, 1932, vol. 206, p. 126.
104. A. SCHNEIDER and E. HESSE : *Zeitschrift für Elektrochemie*, 1940, vol. 46, p. 279.
105. H. A. SHADDUCK : *Journal of Physical Chemistry*, 1937, vol. 41, p. 625.
106. C. H. SHOMATE : *Journal of the American Chemical Society*, 1946, vol. 68, p. 1634.
107. C. H. SHOMATE, *Ibid.*, 1946, vol. 68, p. 964.
108. C. H. SHOMATE : *Ibid.*, 1947, vol. 69, p. 220.
109. C. H. SHOMATE : *Industrial and Engineering Chemistry*, 1944, vol. 36, p. 910.
110. C. H. SHOMATE and B. F. NAYLOR : *Journal of the American Chemical Society*, 1945, vol. 67, p. 72.
111. C. H. SHOMATE, B. F. NAYLOR, and F. S. BOERICKE : *United States Bureau of Mines*, 1946, *Report No.* 3864.
112. P. E. SNYDER and H. SELTZ : *Journal of the American Chemical Society*, 1945, vol. 67, p. 683.
113. J. C. SOUTHARD : *Ibid.*, 1941, vol. 63, pp. 3142, 3147.
114. J. C. SOUTHARD and R. T. MILNER : *Ibid.*, 1935, vol. 57, p. 983.
115. J. C. SOUTHARD and G. E. MOORE : *Ibid.*, 1942, vol. 64, p. 1769.
116. J. C. SOUTHARD and C. H. SHOMATE : *Journal of the American Chemical Society*, 1942, vol. 64, p. 1770.
117. C. R. TAYLOR and J. CHIPMAN : *Transactions of the American Institute of Mining and Metallurgical Engineers*, 1942, *Technical Publication No.* 1499.
118. J. THOMSEN : " Thermochemische Untersuchungen," 1883, vol. 2. Leipzig.
119. T. THORVALDSON, W. G. BROWN, and C. R. PEAKER: *Journal of the American Chemical Society*, 1930, vol. 52, p. 3927.
120. T. THORVALDSON, W. G. BROWN, and C. R. PEAKER: *Ibid.*, 1929, vol. 51, p. 2678.
121. T. THORVALDSON, R. R. EDWARDS and E. C. BAILEY : *Zeitschrift für anorganische und allgemeine Chemie*, 1938, vol. 236, p. 310.
122. C. E. TILLEY : *Mineralogische petrographische Mitteilungen*, 1933, vol. 43, p. 414.
123. D. R. TORGESON and T. G. SAHAMA : *Journal of the American Chemical Society*, 1948, vol. 70, p. 2156.
124. D. R. TORGESON and C. H. SHOMATE : *Ibid.*, 1947, vol. 69, p. 2103.
125. G. TRÖMEL and H. SCHNEIDERHÖHN : *Mitteilungen aus dem Kaiser-Wilhelm-Institut für Eisenforschung*, 1932, vol. 14, p. 25.
126. H. TROITZSCH : Dissertation, Braunschweig, 1936.
127. M. D. TSCHERNOBAEFF : *Revue de Métallurgie*, 1905, vol. 21, p. 729.
128. E. VOOS : *Zeitschrift für anorganische und allgemeine Chemie*, 1935, vol. 222, p. 213.
129. H. WAGNER : *Ibid.*, 1932, vol. 208, p. 1.
130. W. P. WHITE : *Journal of the American Chemical Society*, 1933, vol. 55, p. 1047.
131. J. WHITE, D. D. HOWAT, and R. HAY : *Journal of the Royal Technical College, Glasgow*, 1933–36, vol. 3, p. 239.
132. S. WOLOGDINE : *Comptes Rendus*, 1913, vol. 157, p. 121.
133. S. WOLOGDINE and B. PENKIEWITSCH : *Comptes Rendus*, 1914, vol. 158, p. 498.
134. R. W. G. WYCKOFF : " Crystal Structures," Section 1. 1948, New York: Interscience Publications, Inc.



IRON AND STEELWORKS ENGINEERING

THE IRON AND STEEL ENGINEERS GROUP

THE IRON AND STEEL ENGINEERS GROUP

REPORT OF THE TWELFTH MEETING

THE TWELFTH MEETING OF THE IRON AND STEEL ENGINEERS GROUP of The Iron and Steel Institute was held at 4 Grosvenor Gardens, London, S.W.1, on Thursday, 23rd March, 1950. Mr. W. F. CARTWRIGHT (Steel Company of Wales, Ltd.), Chairman of the Group, was in the Chair, except for a short period at the end of the Afternoon Session, when his place was taken by Mr. W. J. POOL. The AFTERNOON SESSION was devoted to the presentation and discussion of two papers entitled "Structural Frames for Melting Shops," by J. S. TERRINGTON (B.I.S.R.A.), published in the September, 1950, issue of the *Journal*, and "A Proposed Method of Specifying Travel-Motion Performance for Steelworks Overhead Cranes," by D. A. WISE and L. N. BRAMLEY (B.I.S.R.A.).

PROCEEDINGS OF PART OF THE AFTERNOON SESSION: 2.0 P.M. to 4.30 P.M.

Discussion on the Paper—

A PROPOSED METHOD OF SPECIFYING TRAVEL-MOTION PERFORMANCE FOR STEELWORKS OVERHEAD CRANES*

Mr. **D. A. Wise** and Dr. **L. N. Bramley** briefly introduced their paper.

Mr. **W. F. Cartwright**: As the Chairman of the Sub-Committee of B.I.S.R.A. which worked on the crane specification, I am naturally very interested in this paper, which is the main outcome of the deliberations.

The authors have gone a long way towards stopping people thinking in a groove in regard to specifications for cranes. Even today it is quite common for people to have a new crane and then to discover that its performance is not satisfactory, although there is already in the same building a crane that has a satisfactory performance.

Unfortunately, I have to leave shortly for another meeting and I will hand over the chairmanship for the remainder of the meeting to Mr. Pool, who is a member of the Engineering Committee.

(*Mr. W. J. Pool then took the Chair.*)

Mr. **R. A. West** (Igranic Electric Co., Ltd.): There are many figures in this paper upon which people can base their opinions and I am sure that the formidable task undertaken by the authors has been tackled on the right lines. I believe they want our opinions on their choice of classification, so that they may be assured of some measure of agreement before proceeding further with their investigations.

Some years ago I tried to write a small book on this subject but it was very difficult to find anybody in the steel community who would say, "That is what we want." Ultimately I was largely influenced by what the drivers wanted, because a high-speed crane is useless unless there is adequate acceleration and braking.

The authors are definitely correct in trying to obtain a classification that is simple and that can be checked on site. But I doubt whether the classification is sufficiently simple. Admittedly the only thing they could do in the circumstances was to test all the motions unloaded, because it is very difficult to make proper tests under full load. One must therefore be careful to temper the conclusions drawn from such methods, particularly in the case of cross-traverse motions where the unladen/laden weight ratio may be very low.

I should like to put forward some thoughts which have occurred to me since my book was written; these thoughts have been stimulated by the authors' data.

Firstly I have some queries on their figures. Considering that all the cranes were tested unloaded, it is difficult to understand the low acceleration of some of them. For example, item 20 in Table I was a 115-h.p. motor, which gives a rated tractive effort of 135 lb./ton light and 89 lb./ton laden; that is a fairly high rating. Under item 24 there is a rated tractive effort for the 98-h.p. motor of 224 lb./ton light and 117 lb./ton loaded; that is high, too. I find it very hard to see why the acceleration is low. It is definitely classed as a low-duty job from the point of view of acceleration (and speed, which is of no interest in the present context). Under item 23, where there are two 20-h.p. motors, the figures are 39 lb./ton rated tractive effort laden and 86 lb./ton light—and 86 lb./ton light is still quite a bit; but it is a little easier to understand when the rated tractive effort is low, why the acceleration produced is also low under

* *Journal of The Iron and Steel Institute*, 1950, vol. 164, April, pp. 439–451.

test. Does the proportion of the total inertia represented by the motor account for this ?

I will give a few more figures that I have actually been working on. For a 50-h.p. A.C. motor, applied to four different classes of traction duty—100 ft./min., 200 ft./min., 400 ft./min., and 500 ft./min. geared speeds—the ratio of the inertia of the motor and brake pulley to the inertia of the linear movement converted to the high-speed shaft was 10% at 500 ft./min., 12% at 400 ft./min., 21% at 200 ft./min. and 42% at 100 ft./min. In my book I assumed an average figure for rotational inertia of 10% added to the linear inertia, but that is only satisfactory for D.C. drives in the region of 300 ft./min. geared speed.

It might help if the authors could later investigate the Wr^2 features of some of these cranes. It is possible that on these very low-speed cranes the stored energy of the motor is such a large proportion of the total stored energy that it is, in fact, acting as a useful 'fly-wheel' and is controlling the acceleration.

A more direct comparison should be made between the classification suggested by the authors and that which was fundamental to the development of my book. Figures 17, 21, 22, 23, 24, and 25 in the latter all cover a range of geared speed from 100 to at least 600 ft./min. and all have suffix numbers 1, 2, or 3 to indicate the classification corresponding to Figs. 15 and 16, namely, accelerations of 2·0, 1·5, and 1·0 ft./sec./sec., respectively. It is intended that the rated tractive effort should be mandatory when the acceleration has been chosen. The horse-power/ton curves of Figs. 21 to 25 are given to enable a rapid calculation of a frame size suitable for the crane to be made in the drawing office ; the frame is chosen from the schedule provided by the motor maker or the user, and the method of using these curves is detailed in Chapter IX. The question of geared speed is not fundamental to my classification ; it is left to the discretion of the person who applies the curves. Consequently,

West Class 1	covers	Bramley and Wise	Classes 1 and 2
„ Class 2	„	„	„	„	Classes 3 and 4
„ Class 3	„	„	„	„	Class 5

As an example, a crane with high acceleration and high geared speed would require a power for the motor which is considerably greater than is normal in this country although fairly common in America. Consequently it is my belief that this super crane is seldom necessary and I was hesitant in making suggestions as to crane classifications in the early part of my book (p. 11). It was recommended that a high speed is not necessary when 2·0 ft./sec./sec. is adopted, but that at least 1·5 ft./sec./sec. is required for cranes having a high speed. I am afraid I did not make an adequate distinction between these suggestions and the freedom to choose any geared speed which is apparent in the subsequent data. I am sorry if this has led to confusion.

Reflection on the crane builders' recommendations and the methods of using cranes in steelworks has now led me to another point of view on this question of acceleration which the authors may wish to consider in their later deliberations. With a few exceptions, the allocation of a class and proper long-travel design to the fully loaded crane results in all cranes having approximately class 1 performance when unloaded ; *e.g.*, my class 1, with 2 ft./sec./sec. It might be worth while to investigate the results obtained by designing for class 1 unloaded, to check the performance with full load, and then to set the contactor gear to give this performance on load. Then, although the contactor gear has been set a little slower to deal with the full-load condition and to prevent the driver from rushing off with the full load, the fact that the crane is unloaded, will provide nearly 2 ft./sec./sec. acceleration. Starting from that basis it might be possible to arrive at a means of classifying crane long-travel motions which is really just one class with a few exceptions which obviously engineering talent must bring out.

With plain bearings plug braking is adequate for both light and full loading, but with anti-friction bearings the method needs investigation as the braking may be too sluggish ; that is to say, if the suggestion of rating everything on the unloaded condition and then letting the loaded condition follow suit naturally, is adopted.

There is usually no need and seldom any desire on the part of the drivers to use class 1 acceleration and braking except when the crane is lightly loaded. This also agrees well with the unladen/laden weight ratios which are common parameters of the various types of crane.

On the cross-traverse motion the acceleration is probably not very important because the speed is usually low, except in the case of special-duty machines. The usual crane builder's figure of 80 lb./ton loaded gives satisfactory results in all cases up to 150 ft./min., because the overload capacity of the motor can cope with inertia loads. Care is necessary to give adequate braking without skidding.

Satisfactory braking on cross-traverse when unloaded can only be achieved, or an occasional misfit avoided, by a very careful design of the resistor layout. There is generally little trouble in stopping the trolley by plugging, perhaps because of the high proportion of total inertia that is represented by the motor armature ; it acts as a useful kind of fly-wheel in preventing the speed from changing too quickly. However, there may be trouble under extreme conditions, as, for example, when a trolley weighs about 7 or 8 times as much with the full load on it as when it is empty. In such cases it is essential for the crane builder to give the control gear maker details of the weights, the geared speed, and the Wr^2 of the high-speed parts so that he can design his resistor layout accordingly.

Mr. **D. A. Wise** and Dr. **L. N. Bramley** said in reply : It might be useful to add some further figures to those quoted by Mr. West relating to the effect of rotational inertia on the initial acceleration of cranes. In the symposium on equipment for mill-crane bridge drives,* Mr. J. A. Jackson quoted a figure of 4% on cranes with small gear reductions and 7% on cranes with large gear ratios to be added to the linear inertia to take account of rotational inertia. These figures are smaller than the figure of 10% mentioned by Mr. West.

We suggest that a possible cause of low acceleration might be that someone had interfered with the setting of the control gear. We found several examples of this in our tour round the steelworks. There is also the possibility of high tractive resistance in certain cases, especially from rest. There seems to be little information on this subject. Mr. West, in his book, quotes 25 lb./ton as the tractive resistance for plain-bearing cranes. The American Crane Specification uses 24 lb./ton, and during some of the crane tests, when approximate values of tractive resistance were assessed, we obtained values ranging from 10–35 lb./ton, averaging about 25 lb./ton.

Mr. West suggested that there might be just one class for acceleration in the case of unloaded cranes, on the assumption that there is not very much difference between the initial slopes of the curves shown in Fig. 10.

* *The Iron and Steel Engineer*, 1940, vol. 17, Nov., pp. 34–62.

Although this new suggestion by Mr. West is most interesting, and may have possibilities, it does not appear to be borne out by the curves shown in that figure.

We do not really agree with the way Mr. West wishes to line up our classes with his own ; his class 1 does not include what we call our super class. On arriving at a steelworks we asked to test the cranes which we considered to be giving a good performance ; and the ones which really were the ' apples of the eyes ' of the steelworks managers were the ones which turned out to be our super-class cranes. They are better than Mr. West's class 1 and production would have suffered if their performance had been lower. We thus still consider that Mr. West's class 1 corresponds to our class 2, that his class 2 corresponds with our class 3, and that his class 3 is very largely our class 5.

It cannot be emphasized too much that the proposed classification can be followed by any steelworks engineer with nothing more than a tape measure, a stop-watch, and a tachometer. With those simple things he can classify any one of his cranes. This is probably a good thing, because if lengthy or complicated tests were necessary to find out how existing cranes were performing, so that new ones like them, or better or worse than them, could be ordered, the work would never get done. Therefore, we have had to keep the test very simple, and we feel that this is our chief justification for not making it complete.

We would have liked to have taken braking into account, but it was one of those things which had to be neglected if the job was to be done at all. We think that most people will agree that braking is not so much in dispute as acceleration.

Mr. **E. C. Davies** (General Electric Co., Ltd.) : I wish to make a plea for an extension of the analysis of crane performance to enable the operating duty-cycles to be predicted with at least a reasonable degree of accuracy.

This aspect is naturally of particular importance to the motor manufacturer, but as standardized steelworks-type series-wound mill motors are used for these drives in the majority of cases, the problem also affects the travel-motion performance of the crane because :

1. The speed of such motors when loaded at their nominal one-hour rated current is standardized, and in the interest of all concerned it is desirable to adhere to these standards.
2. As the authors have stated, the speeds of these series motors are very sensitive to changes of load ; *e.g.*, at half the rated load the speed would be 40–50% higher than at rated load.

It follows, therefore, that as the nominal rating of the motor must be determined by its operational duty-cycle, motors having differing ratings would operate on a given crane at greatly differing speeds when approaching the balancing portion of the speed/time curve, even if the speeds at their nominal ratings were approximately equal.

Thus it will be appreciated that to predict the performance of a crane motion, the nominal rating of the motor should first be determined by the operating load-cycle and the number of cycles per hour. Having selected the size of motor required, from thermal considerations, it is then possible, by reference to the load-speed characteristic of the machine, to check its speed on reduced loading in the region of free running. Only then may the gear ratio be selected to give the required travel speed which the authors have naturally chosen as one of the two main criteria that determine crane performance.

Mr. **Wise** : We are glad that Mr. Davies has brought up the subjects of duty-cycles and motor application. These are important matters and are now receiving further attention within B.I.S.R.A.

To enable an engineer to design a travel-motion drive he should have :

(*a*) the mechanical characteristic required (*i.e.*, the complete speed/time curve)
(*b*) some indication of the time taken for individual moves and the frequency of these moves (operational duty-cycle).

The paper presents a method for specifying the mechanical characteristic of a motion ; but, as Mr. Davies has indicated, data on operational duty-cycles are also required before the most satisfactory motor application can be made. It is perhaps because of inadequate specification of performance, both in respect of duty-cycles and the mechanical characteristic, that crane makers have been forced to rely largely on past practice and guesswork in motor application.

Performance specification according to duty-cycle is covered on p. 439 of the paper, which indicates the lack of knowledge on the subject of duty-cycles in steelworks drives.

Mr. Davies outlines a method of motor application from motor-heating considerations and we agree with the principles involved. Presumably, after the motor size and gear ratio are obtained the motor control gear is chosen so that requisite initial acceleration is obtained, and the drive is then checked to ensure that the torque demands from the motor are not above its capacity.

Dr. **Bramley** : We should like to add one point of general interest. Referring to Fig. 10, it can be seen that the constant-distance bands at 8 ft., 40 ft., and 100 ft. are a good illustration of the relative importance of acceleration and speed with varying distance. Symbols lying to the left of these bands represent cranes having high initial accelerations, whereas symbols to the right of the bands represent cranes having low initial accelerations (for approximately the same speeds). Thus it may be seen that changing the initial acceleration of a crane, having a given speed at a given distance, can make a difference of only 2–3 sec. in the time taken to travel that distance, whereas one crane may describe 100 ft. in 13 sec. and another with a lower speed may take 21 sec. Thus for distances of 100 ft. speed is predominantly important, whereas for short distances initial acceleration becomes important. This point is not sufficiently emphasized in the paper.

Mr. **J. A. Broughall** (British Railways) : We are at the moment drawing up a Standard Railway Specification for Electric Cranes and I view the matter in the light of my knowledge of electric traction. The problem seems to be fundamentally the same ; namely, the carrying of a certain load from one place to another in a certain time, depending on the requirements of the job.

The authors have written an interesting epitome of the problem of defining speed that arises in electric traction schemes. Like them, we are interested in initial acceleration as well as the maximum speed, and the method they propose seems to be a very convenient one for expressing these quantities in practical terms. The question of retardation deserves investigation along similar lines.

The absence of information concerning track resistance is also noticeable in railway practice, especially in connection with the movement of heavy loads at slow speeds as, for example, in specifying the performance required of diesel electric shunters. We also have difficulties

similar to those of crane makers in regard to interference between the wheels of the crane carriage and the crane rails, and we have to find an equitable method of specifying the obligations of those who design and install the crane rails and the crane respectively.

Mr. **H. S. Carnegie** (English Electric Co., Ltd.): There is also another way of looking at the same problem. Firstly, the maximum value of the acceleration is a function of the torque capabilities of the motor. If it is not exercised, that is not the motor's fault; it is still there to be utilized. Secondly, the speed of the crane is related to the full-load speed. With those two determined, the power of the motor is then definitely fixed, omitting the question of rating referred to by another contributor to the discussion. This, again, is borne out by taking the authors' groups in Table I—high, medium-high, and so on—and taking the horse-power per ton. They seem to fall naturally into three classes. Obviously the high-medium and the medium-high should have about the same horse-power per ton.

Cranes driven by mill-type motors seem to have a motor inertia of about 10% of the total for high-speed cranes rising, as Mr. West mentioned, to about 30–40% of the total for low-speed cranes.

Mr. **West**: The relative values of rotational and linear inertia do not change inversely as the square of the geared speed, since a given motor frame size will be able to drive a heavier crane in the lower geared speed, and therefore the inertia ratio varies inversely as the geared speed.

It is as well to clarify the basis of these comparisons. If one frame size is put on a number of different cranes for which it is equally suited, each having different geared speeds, then the ratio of the rotational inertia varies inversely as the geared speed, and in direct proportion to the tractive effort. The motor may be changed from crane to crane by retaining a uniform lb./ton tractive effort throughout and by varying the tonnage, but in practice this should not be done, if heating is considered. Working on the basis of an A.C.-motor and middle-duty crane, a 100 lb./ton tractive effort is suitable for a geared speed of 100 or 200 ft./min., but this must be increased to 120 or 130 lb./ton if the motor is to remain reasonably cool at a speed of 400 or 500 ft./min.

Neglecting gearing efficiency (which complicates the problem) the ratio of motor inertia to linear inertia varies in proportion to tractive effort and inversely as the geared speed.

Mr. **J. Nelsey** (McLellan and Partners): I do not think the proposed specifications are comprehensive enough, and one or two other speakers, particularly Mr. Davies and Mr. Carnegie, have concurred in that view.

The authors have said that it is not possible for the majority of steelworks to consider the duty-cycle. Not only do I feel that it is possible but (and I feel that this is fundamental) it is desirable in the majority of cases that it should be done—desirable because a motor may satisfy the torque requirements of the drive and yet be seriously overheated in performing the duty required of it.

In talking of duty-cycles, one meets the problem of a crane which has to travel considerable distances in a short time, and very short distances also in a short time, and while a minimum of time is a common factor in both cases the requirements on the motor are vastly different. However, that is not important because from a study of the duty-cycle of any one crane for a whole day, it is possible to derive the total kilowatt hours of work that have to be done by the motor, and by taking the worst hour it can be seen whether the motor would be overheated in that time. Better still (here I do not agree with Mr. Davies) the motor ratings could be revised to conform more closely with practical requirements, because the present half-hour and one-hour ratings do not.

There is apparently to be no limit to top speed or balancing speed. On p. 440, the authors state that the balancing speed is seldom attained. In my opinion balancing speed is often attained. I do not think it will be denied that in the length of building available it could be attained in most cases, and this fact would justify the inclusion of top-speed limitation in the specification. In any case, if the purchaser gets a higher speed than he wants it is almost certainly at the expense of acceleration, and he is not getting the best value for his money.

I should like to make a plea for a standard means of calculation of the performance of standard types of crane, possibly on the lines put forward by Mr. Skeehan,* with perhaps a good deal more attention paid to acceleration, as suggested by Mr. West. We should not try to express it quite so simply as in the A.I.S.E. specification for long-travel motions with sleeve bearings, because that does not accurately relate horse-power and speed.

On p. 441 of the authors' paper the exclusion of deceleration is justified by saying that efficiency of braking in modern cranes is in little doubt. I consider that this leaves a loophole, especially where accurate load spotting is required (for example, on a ladle crane when teeming). The performance here should be tied down to the last detail.

On p. 443 it is stated that "As far as possible only cranes which the production personnel considered were giving satisfactory performances were tested." One is led to conclude that this specification is based on opinion rather than on facts; in other words, that existing standards of performance are considered to be ideal. This is surely not so, and I feel that it would be worth while to employ mathematical analysis to determine whether the combinations of acceleration and deceleration give the best possible output in tonnage.

I would like to suggest what appears to me a more rapid method of recording the speed and acceleration of a crane. One could replace the cine-camera with a cathode ray oscilloscope so connected as to produce a 'blip' of light on the screen whose vertical ordinate is proportional to the potential across the terminals of a tachometer on the motor shaft, and whose time base is arranged so that the spot of light traces a speed/time curve on the screen. If squared transparent paper is placed over the screen, an observer could plot the curve with a pencil as the light spot moves. It would then be a simple matter to convert the r.p.m. curve so obtained to the more conventional curve showing feet per minute.

Dr. **L. N. Bramley**: In regard to the duty-cycle being the best method, we have really two aims. First, we are trying to get the crane buyers to specify performance and to let the crane makers produce a crane which will give that performance. Secondly, we are trying to get the crane makers to accumulate design data on only a few classes of cranes so that in a few years' time they will be able to say, for instance, "A class 3 crane is needed here; we have designed half a dozen of those in the last year and we know what is required."

* *The Iron and Steel Engineer*, 1947, vol. 24, Dec., pp. 83–88.

As to the balancing speed being seldom attained, all the curves in Fig. 10 still have a very perceptible slope upwards up to 25 sec. At the Abbey works there are a large number of very long shops, but they are not all fully equipped with their correct numbers of cranes; and so, although balancing speed will be attained more often than is usual, I do not think it will be attained very frequently. It may be obtained fairly often in one particular shop at the Abbey works because it is very long and the cranes have been designed to be rather slow.

We agree that braking is important on ladle cranes. It should be possible to stop the crane very gently so as not to spill the contents of the ladle. Severe braking would be disastrous.

Mr. Nelsey referred to the fact that we had used only good cranes. A start had to be made somewhere. We tested about 70 cranes and felt that if the best cranes were tested, at least it would indicate the type of performance that is available today. There is no reason why a crane that is better than any one of the classes defined should not be specified, but it should be done on the basis of duty-cycle. The BISRA Specification makes full allowance for following the duty-cycle method in specifying cranes.

There are several factors against using a C.R.O. on the travel motion to define the characteristics. Most of the cranes tested were available at very short notice and for only a few minutes and were approached by vertical steel stairways, so that equipment installation was severely limited. The alternative would have been to use a small oscilloscope, but then the curve plotted on the screen would have been too small. Vibration would be severe, and I do not think we would have been able to follow the spot on the scale, although a photographic technique might eliminate this difficulty. A further difficulty would be obtaining an A.C. supply to operate the C.R.O. on top of a D.C. crane. These elaborate techniques would have given more accurate results, but we should have tested only a dozen cranes instead of 70, which was barely enough.

Motor rating is important in crane design and is inextricably bound up with duty-cycles and crane performance. Mr. Wise is looking into the possibilities of producing more evidence on motor rating. I have no doubt that as a result of that we shall be able to improve our outlook on specifying travel-motion performance.

Mr. **J. Russell Taylor** (Igranic Electric Co., Ltd.): A low-acceleration high-speed crane, if slowed down and stopped by plugging, will generally have a poor retardation. This will make driving difficult because the driver must begin to stop well away from the stopping point. A crane with good acceleration and consequent good plugging may be driven at top speed much nearer the stopping point and so becomes much easier to drive and gives more accurate spotting.

As an illustration a number of cranes in a South Wales steelworks were geared to 750 ft./min. and driven by two motors in parallel. The horse-power was definitely low. A test from stop to stop over 200 ft. gave a time of 32 sec. and a most indefinite stop position. With both motors connected in series, thus halving the geared and free-running speeds, the stop-to-stop time for 200 ft. became 29 sec. and the stopping position was very accurate. The difference in time and spotting was due to the much greater ease of judging distance at half speed.

This experiment shows why some cranes are never driven at top speed—the driver is afraid of overrunning his stopping point.

I am convinced that in the past the advantages of acceleration have been overlooked and extra performance has usually been expected to mean higher geared speeds. I hope that the present paper will help to emphasize the advantages of acceleration.

CORRESPONDENCE

Mr. **A. Hunter** (The United Steel Companies, Ltd.) wrote: In my opinion the most valuable part of this paper is Table I on p. 442. If these data could be established for the cranes in each works the selection of long-travel drives would become based on measurable terms, rather than on subjective judgment of 'good' or 'bad' cranes.

The necessity for a classification as described by the authors is less clear to me. Having reduced travel motions to exact terms there seems to be nothing to be gained by selecting arbitrary ranges as 'fast,' 'slow,' etc. If data such as those shown in Table I were available to engineers contemplating additional cranes there would be very much less excuse for not providing the design data on a duty-cycle basis.

The authors' classification may very well be adopted as props to support indifference to a more precise statement. This is particularly dangerous when the props have the inherent weaknesses which I think they have.

The basis of the classification is stated (p. 441) to be (*a*) initial acceleration and (*b*) the speed attained after a certain time. However, the acceleration regarded by the authors as the criterion is only truly 'initial' fortuitously. If the initial acceleration had been defined (as in A.I.S.E. Standard No. 6) as the acceleration up to the point at which the motor comes off the resistors, it may have been possible to dispense with the double criteria of acceleration and speed and to have adhered to a criterion of true initial acceleration. Other things being equal, the balancing speed and the speed at any instant after rest is primarily dependent upon the true initial acceleration. The criterion of true initial acceleration also has the additional advantage of being of direct and immediate use to motor and control-gear designers.

The A.I.S.E. Standard suggests that accelerations up to 0·5 ft./sec./sec. are slow, 0·5–1·5 ft./sec./sec. are medium, and 1·5–2·5 ft./sec./sec. are fast, but there is no fixed standard classification such as is proposed in the present paper. Engineers are required to state the initial acceleration desired. With the help of data obtained in the manner described by the authors there is now no reason why they should not be able to specify it and we must not invite criticism from uninformed quarters by putting engineers into the position of signing a specification for a 'mediocre' or class 4 crane.

Mr. **D. A. Wise** (in reply): As the methods proposed in this paper for dealing with travel-motion performance have been compared with those used in the American Specification, the differences between the two methods should be stated. Both specifications agree that where a definite duty-cycle is available, the drive should be designed to comply with that duty-cycle. However, where insufficient duty-cycle details are available then:

(*a*) The BISRA Specification requires the purchaser to specify performance in terms of the simple criteria given in the paper. The choice of motor size and gear ratio is left entirely to the crane designer.

(*b*) The American Specification requires the purchaser to specify initial acceleration (*i.e.*, acceleration on resistor) and speed of the motion. The Specification then gives a standard procedure for determining motor size and gear ratio from the specified information.

We cannot see how travel-motion performance can be adequately specified by initial acceleration alone.

Even with initial acceleration defined as in the American Specification, it will be noted that this Specification also calls upon the purchaser to specify speed.

For the purposes of the travel-motion design and for the purposes of the American Specification, it is advantageous to specify initial acceleration as that occurring while the motor is on resistor, but we do not think this is appropriate to the proposals given in the paper, since the simple test to assess initial acceleration (that is, timing the motion from rest over a distance of 8 ft.) would no longer be applicable.

We cannot agree with the statement that, other things being equal, the balancing speed of a travel motion depends on initial acceleration. The balancing speed of a given travel motion is fixed when the motor size and gear ratio have been fixed, and the initial acceleration can then be varied within wide limits by altering the motor control gear.

With regard to engineers being subject to criticism for the specification of a 'mediocre' or class 4 crane, perhaps the choice of the word 'mediocre' is unfortunate on our part. This word is not used in the final performance table (Table III) included in the BISRA Crane Specification and is used in the paper merely as a comparative term.

Mr. **G. V. Sadler** (The Vaughan Crane Co., Ltd.) wrote: The information given in this excellent and informative paper is extremely useful for crane makers who are always anxious to find a real basis through which they may interpret their customers' needs for particular cranes.

In addition to the information given, however, from a crane maker's point of view it would be very useful to have certain additional information in connection with the tests taken, although I realize that the time available on most of the cranes was very short. For instance, in Table I, does the figure of unladen weight refer to the whole crane or to the girders without the crab, and have the authors any figures of the span of the cranes on which the tests were taken, and also the approximate age of the cranes?

With regard to Table II, is it a fact that each crab tested is fitted with only one hoist motion, or was there a main and an auxiliary hoist motion on some of them? It would be interesting to know, also, at what part of the crane bridge the crab speeds were tested, since on some cranes the camber of the girders has some effect on the crab speeds. Can the authors state what type of timing relay was used for accelerating the cranes on test? also, could the make of control gear be classified by letters in the same way as the crane makers?

If any further tests of this nature are undertaken, it would be of great value if some electrical figures could be provided, such as might be supplied from a recording ammeter in the motor circuit during the tests. Concerning the question of high acceleration on long-travel motions, it would be interesting to know how closely the maximum allowable torque output of the motors is approached during the acceleration period, and also the effect of this high acceleration on the power supply to the crane, together with a figure for the power losses in the resistors.

An analysis of electrical readings, if they can be made available, would enable the crane designer to have an even clearer picture of what is involved in accelerating the long-travel motion on cranes, than is already available from the paper, and it is hoped that the authors may be able to provide this information in future tests.

Mr. **D. A. Wise** (in reply): The unladen weights given in Table I refer to the whole crane. The spans of the cranes tested would have to be collated from the steelworks visited. Concerning the other information requested, the following may be of interest:

Date of Manufacture

Table I

Date	Reference	Date	Reference
1907	30	1936–1940	2, 5, 7, 16
1911–1920	14, 22		20, 21, 24, 33
1921–1930	1, 19, 28	1941–1945	9, 17, 18, 26, 31
1931–1935	3, 6, 23, 27	1946–1948	4, 8, 10, 11, 12, 13, 25, 29

Table II

Date	Reference	Date	Reference
1911–1920	8, 20, 23, 30	1936–1940	14, 18, 33–35
1921–1930	1, 7, 12	1941–1945	13, 15, 25
1931–1935	3–6, 10, 19, 21, 24, 26, 28	1946–1948	2, 9, 11, 17, 27, 29, 31, 32

Type of Acceleration Control

Table I

Control	Reference
Time-limit	3, 7, 8, 10, 11–13, 17–22, 24, 25, 29, 31–33
Current-limit	1, 2, 5, 6, 15, 26
Drum	4, 9, 14, 23, 28, 30

Type of Control

Table II

Control	Reference
Contactor	1, 2, 4–7, 10, 11, 14–18, 21, 22, 26–35
Drum	3, 8, 9, 12, 13, 19, 20, 23–25

During the testing of the cross-travel motions the crab was started from one end of the span and proceeded until either the balancing speed was reached or the crab approached the other end of the span. A return journey was then made, and in most cases the curves in Figs. 17 and 18 are averages taken from two runs such as these.

The suggestions for further tests are appreciated, and tests on these lines may be carried out at a later date to provide information that will assist motor application to steelworks auxiliary drives.

Mr. **H. H. Broughton** (Consulting Engineer, Cheam) wrote: The authors have made a long-overdue attempt to rationalize the preliminary work involved in the design or rating of the travelling and traversing motions of D.C. overhead cranes. Had A.C.-operated motions been included in the analysis I believe that a decisive answer would have been furnished to a question which has given rise to a good deal of discussion in the past. It is, I agree, unsatisfactory to consider travel-motion performance in terms of geared speed when the driving motor is operated under nameplate rated output; yet the balancing speed is probably more important than the speed attained, or the distance travelled, in a relatively short time.

The value of the comprehensive data embodied in Tables I and II would have been enhanced had the total travelling and traversing distances been included because the solution of the problem is governed by those distances.

From these data and from Fig. 10, it is evident that in some cases the motions could be improved by altering the gear ratio and by reducing the size of the driving motor.

The tables and curves brought to the fore the question of balancing speed. Thus the crane, reference 1, which had a geared speed of 352 ft./min., attained a speed of 528 ft./min. in 10 sec. Had the motion been allowed

to continue, a speed of about 700 ft./min. would have been reached and, in consequence, the severity of the braking duty would be quadrupled. It has been shown that marked improvement can often be effected by altering the gear ratio to a value based on motor speed under balanced running conditions, and I suggest that, as a basis for design, the rated speed of the motion should be regarded as 95% of the balancing speed. The odd 5% is of no moment and its elimination helps to simplify the work. Can the authors confirm that the inclusion of the balancing speed requirement will not vitiate their proposal? The use of contactor control gear allows variation in the rate of acceleration between wide limits, and on that account the elaborate classification given in the paper is thought to be unnecessary. The five groups into which cranes are sometimes divided to suit service conditions is desirable for structural reasons. The introduction of 'type curves' into a modified Fig. 10 would be helpful to designers wishing to give effect to the authors' proposals.

Mr. **D. A. Wise** (in reply): Our tests show that balancing speeds were seldom reached in the unloaded conditions, and we did not feel justified in extrapolating the curves in order to arrive at balancing speeds.

If a criterion of balancing speed could be added to the criteria given in the paper we feel that this would improve the definition of the form of the speed/time curve for the various classes of long-travel motion (*i.e.*, 1, 2, etc.). This, however, would inevitably lead to still more classes of cranes and, on these grounds, could not be justified.

Although we agree that the use of contactor control gear enables the initial acceleration to be varied between wide limits, we cannot see why this fact should make the classification unnecessary.

The knowledge of trip-distances of the various cranes listed, particularly for long-travel motions, would be of the utmost value. However, the trip-distance for the long-travel motions of many steelworks cranes is a variable quantity, and the determination of a figure representative of the average trip-distance for most motions would have involved further tests with statistical interpretation.

The alternative proposal for specifying travel-motion performance (*i.e.*, the production of a 'type' speed/time curve corresponding to the 5 classes of long-travel motion, with presumably an allowable tolerance on each curve) was considered, but it was finally decided not to adopt it since it would have meant going appreciably beyond the limits of Tables III and IV. A further disadvantage is that the method does not appear to lend itself to simple acceptance tests.

Returning to Mr. West's and Mr. Carnegie's comments on the subject of the effect of motor inertia on crane performance, the following extra figures may be of interest:

Take the case of crane No. 24 in Table I (mentioned by Mr. West) and assume for the size of motor used (98 h.p., 1-hour rated) values of 230 and 176 lb.ft.^{2} for the inertias of the motor armature and brake drum respectively. The ratio of the inertia of motor armature and brake drum to linear inertia is given by:

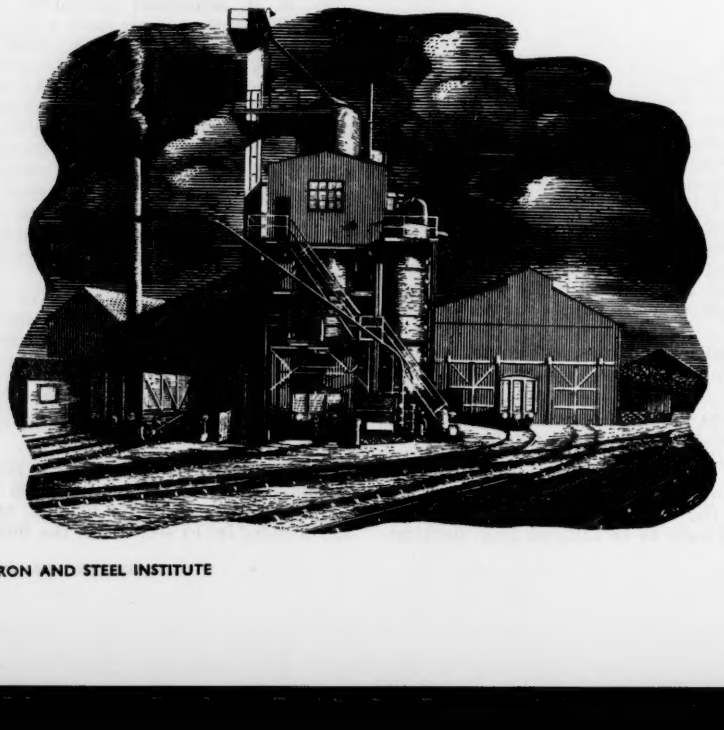
$$\frac{IG^2}{r^2W}$$ where I = inertia of motor and brake drum (lb.ft.^{2})
G = gear ratio
r = radius of road wheel (ft.)
W = weight of crane (lb.)

In this case the ratio is:

$$\frac{406 \times (36 \cdot 6)^2 \times 100}{(1 \cdot 25)^2 \times 2240 \times 130} = 119\%.$$

This is undoubtedly an extreme case and the high ratio explains the very low initial acceleration of this crane. For comparison the inertia ratios for cranes 1, 2, 3, 5, 7, 9, 20, 21 (Table I) have been assessed and were found to be of the order of 18, 15, 8, 5, 9, 13, 26, and 42% respectively.

The remainder of the proceedings—the joint discussion on "Traffic of Iron and Steel Works: A Method of Traffic Analysis," and "Traffic of Iron and Steel Works: The Application of Very High-Frequency Radio Communication"—will be published in the December issue of the *Journal*.



NEWS

ANNOUNCEMENTS AND NEWS OF SCIENCE AND INDUSTRY

THE IRON AND STEEL INSTITUTE
Autumn General Meeting, 1950

The Autumn General Meeting of the Institute will be held on Wednesday and Thursday, 15th and 16th November, 1950, at 4 Grosvenor Gardens, London, S.W.1. The President, Mr. J. R. MENZIES-WILSON, O.B.E., will be in the Chair.

A Buffet Luncheon (price 6*s*. per person) will be arranged in the Institute Library on the Wednesday. There will also be an interval during the morning on both days for light refreshments (no charge).

The programme of the Meeting is as follows :

Wednesday, 15th November, 1950

Morning Session

10.0 to 10.15 A.M.—Formal business.

10.15 to 11.30 A.M.—Joint Discussion on :

"The Thermodynamic Background of Iron and Steelmaking Processes. II—Deoxidation," by F. D. Richardson. (*October*, 1950).

"Studies in the Deoxidation of Iron : Deoxidation by Aluminium," by H. A. Sloman and E. L. Evans. (*May*, 1950).

11.30 to 11.45 A.M.—Interval : Light refreshments in the Library.

11.45 A.M. to 1.0 P.M.—Discussion on "Thermodynamic Aspects of the Movement of Sulphur between Gas and Slag in the Basic Open-Hearth Process," by F. D. Richardson and G. Withers. (*May*, 1950).

1.0 to 2.30 P.M.—Buffet Luncheon in the Library.

Afternoon Session

2.30 to 5.0 P.M.—Discussion on "The Effect of Cold-Work on Steel," by J. H. Andrew, H. Lee, P. L. Chang, B. Fang, and R. Guenot. (*June and August*, 1950).

Thursday, 16th November, 1950

Morning Session

10.0 to 10.45 A.M.—Discussion on "Atlas of Isothermal Transformation Diagrams of B.S. En Steels." (*Special Report No.* 40, 1949).

10.45 to 11.0 A.M.—Interval : Light refreshments in the Library.

11.0 A.M. to NOON—Discussion on : "The Transformation $\alpha \rightarrow \gamma$ and $\gamma \rightarrow \alpha$ in Iron-Rich Binary Iron–Nickel Alloys," by N. P. Allen and C. C. Earley. (Advance copies will be available before the meeting, on request by those intending to be present at the meeting or to contribute to the discussion in writing).

NOON to 1.0 P.M.—Joint Discussion on :

"The Acceleration of the Rate of Isothermal Transformation of Austenite," by M. D. Jepson and F. C. Thompson. (*May*, 1949).

"The Breakdown of Austenite below the M_s Temperature," by F. C. Thompson and M. D. Jepson. (*January*, 1950).

Changes on Council

Mr. G. W. GREEN has succeeded Mr. J. Wilkinson as President of the Leeds Metallurgical Society ; Mr. A. JACKSON has succeeded Mr. H. Henderson as President of the Lincolnshire Iron and Steel Institute. Both have agreed to be Honorary Members of Council during their terms of office.

NEWS OF MEMBERS

▶ Mr. K. A. ALLEN has left the Broken Hill Proprietary Iron and Steel Co., Ltd., to take up an appointment as Lecturer in Organic and Industrial Chemistry at Newcastle Technical College, Australia.

▶ Mr. J. ANDREWS has left Messrs. Colvilles, Ltd., to take up an appointment with Australian Iron and Steel, Ltd., Port Kembla, New South Wales, Australia.

▶ Dr. C. S. BALL has left the Coil Spring Federation Research Organisation at Sheffield University, to take up an appointment as Lecturer in Industrial Metallurgy at Birmingham University.

▶ Dr. B. R. BANERJEE, formerly research engineer at the Standard Oil Co., Chicago, has joined the staff of the University of Calcutta, India.

▶ Mr. A. F. C. BARNES has been awarded the B.Sc. degree and the A.R.S.M. and has left the Royal School of Mines to take up an appointment in the Research Department, Fry's Metal Foundries, Ltd.

▶ Mr. S. BHADURI, recently of the Bhartia Electric Steel Co., Ltd., Calcutta, is recovering from injuries received in a motor-car accident about four months ago. He is convalescing at Raipur, M.P., India.

▶ Mr. D. L. W. COLLINS has been awarded the B.Sc.(Eng.) degree and the A.R.S.M. and has left the Royal School of Mines to take up an appointment as Research Metallurgist, Aluminium Laboratories, Ltd., Banbury.

▶ Mr. R. W. DAWE has transferred to the Laboratory of The Railway Executive, Western Region, at Swindon.

▶ Mr. G. S. DEARNLEY has left Messrs. Parkinson and Cowan, Ltd., to join the staff of the Parkinson Stove Co., Ltd., Birmingham.

▶ Mr. H. K. FARMERY has left the Rogerstone Works of the Northern Aluminium Co., Ltd., to take up a research appointment in the Department of Metallurgy, under Dr. U. R. Evans.

▶ Mr. T. A. HENDERSON has been awarded the B.Sc. degree in Metallurgy of Durham University.

▶ Mr. R. J. C. JAMES has left Messrs. Evered and Co., Ltd., Smethwick, to take up an appointment with Messrs. J. F. Ratcliff (Metals), Ltd., Birmingham.

▶ Mr. D. KERRY has left the Steel Company of Wales, Ltd., to take up an appointment as Deputy Chief

Engineer at the Division of Atomic Energy, Ministry of Supply, Risley.

▶ Mr. D. M. LEWIS has left the British Iron and Steel Research Association, to take up an appointment in the Research and Development Division of the British Steel Founders' Association, Sheffield.

▶ Dr. B. MATUSCHKA has resigned from his position as Managing Director of the Donawitz Steelworks and is now Consulting Engineer to the United Iron and Steel Works, Linz, Austria.

▶ Mr. H. MYKURA has left the British Iron and Steel Research Association to take up an appointment in the Physics Department of University College of the West Indies, Near Kingston, Jamaica.

▶ Mr. E. M. NOYES of Vinyl Products, Ltd., Carshalton, Surrey, has recently met with a serious flying accident. Members will wish him a speedy recovery from his injuries.

▶ Mr. G. K. OGALE has left the Indian Hume Pipe Company and has taken up an appointment in the Department of Metallurgy, College of Engineering, Poona, India.

▶ Dr. E. OROWAN has left the Cavendish Laboratory, University of Cambridge, to take up an appointment in the Mechanical Engineering Department at the Massachusetts Institute of Technology, U.S.A.

▶ Mr. H. W. PAXTON has accepted a Research Fellowship in the Department of Metallurgy at Birmingham University.

▶ Mr. J. N. PRATT, University Research Fellow, has been awarded the Ph.D. degree of the University of Birmingham.

▶ Mr. G. SMELLIE has been appointed Works Manager of the Margam, Port Talbot and Abbey Works. Before these works were centralized, Mr. Smellie was Works Manager of the Margam and Port Talbot Works.

▶ Mr. B. TAYLOR has been awarded the B.Sc. degree in Metallurgy and has left the Royal School of Mines to take up an appointment as a Research Bursar with the British Non-Ferrous Metals Research Association.

▶ Mr. J. THEXTON has left The Mond Nickel Co., Ltd., to take up an appointment as melting-shop manager at Messrs. Henry Wiggin and Co., Ltd.

▶ Major D. J. TONKS has been appointed Engineer (Bridging) under the Chief Civil Engineer, Railways Commission, Perth, Australia.

▶ Mr. S. R. WILLIAMS has left the Ministry of Supply Laboratory, S.T.A.M., to take up an appointment with the Amalgamated Banket Area Gold Company, Tarkwa, Gold Coast Colony, West Africa.

▶ Mr. J. T. WOODHOUSE has been awarded the B.Sc. degree of the University of Leeds, and has been appointed assistant metallurgist with the Park Gate Iron and Steel Co., Ltd.

Obituary

Mr. A. J. HUDSON of South African Farm Implement Manufacturers, Ltd., South Africa, on 5th August, 1949.

Mr. S. WILLIS, of the Tinsley Rolling Mills Co., Ltd., on 9th August, 1950.

Mr. G. W. ALLOTT, formerly General Sales Manager of the Heavy Constructional Division of Messrs. Newton Chambers and Co., Ltd., on 14th August, 1950.

IRON AND STEEL ENGINEERS GROUP

Postponement of Meeting

Owing to the dispute in the printing trade, it has become necessary to postpone the Fourteenth Meeting of the Iron and Steel Engineers Group. The notice appearing in the October, 1950, *Journal* to the effect that the Fourteenth Meeting would be held on the 5th December, 1950, should be disregarded. The revised date for the Meeting will be announced later.

AFFILIATED LOCAL SOCIETIES

Swansea and District Metallurgical Society

A Joint Meeting of the Swansea and District Metallurgical Society and The Iron and Steel Institute will be held at the Central Library, Swansea, on Saturday, 9th December, 1950, at 6.30 P.M. Captain H. J. Thomas, President of the Society, will be in the Chair.

Mr. N. H. Bacon, of the Steel Peech and Tozer Branch of The United Steel Companies, Ltd., Rotherham, will give a lecture on "Ingots Defects."

Liverpool Metallurgical Society

The following Meetings and Visits have been arranged :

1950

2nd Nov.—(Joint Meeting with the Liverpool and District Branch of the Institute of Welding). "*Recent Work of the British Welding Research Association*," by H. G. Taylor.

22nd Nov.—Visit to the Works of Rylands Brothers, Ltd., Warrington, 2.30 P.M.

7th Dec.—"*Research in Deep-Drawing*," by Professor H. W. Swift.

1951

11th Jan.—"*The New Nodular Cast Irons*," by H. Morrogh.

1st Feb.—"*Electrodeposition for Engineering Purposes*," by A. W. Hothersall.

21st Feb.—Visit to the Works of the Manganese Bronze and Brass Co., Birkenhead, 2.30 P.M.

8th March—"*Atomic Structure and the Hardness of Metals*," by Professor Hugh O'Neill.

5th April—Annual General Meeting—Presentation of Prize-winning Student Papers.

23rd May—All-day visit to the Yorkshire Copper Works, Leeds.

All Meetings will be held in the Lecture Theatre, Electricity Service Centre, Whitechapel, Liverpool, and will commence at 7 P.M., with the exception of the Joint Meeting on 2nd November, which will be held at the City Technical College, Byrom Street, Liverpool, at 7 P.M.

Student Paper Competition

The Society has decided to invite the submission of papers, in essay form, from students of metallurgy. The competition is open to all, living or working in the Mersey or Deeside areas, who are engaged upon the full-time study of metallurgy or who had not attained the age of 25 on 5th October, 1950.

The competition is divided into two classes : papers dealing with physical metallurgy and those dealing with an extraction or fabrication process. A prize of three guineas is offered in each class.

Sheffield Society of Engineers and Metallurgists

The following meetings have been arranged :

1950

20th Nov.—"*The Scope and Aims of the Sheffield University Post-Graduate School in Physical Metallurgy*," by A. G. Quarrell.

18th Dec.—Annual General Meeting.

"*Some Technical and Economic Aspects of Industrial Research*," by D. A. Oliver.

1951

22nd Jan.—(Joint Meeting with the Engineers

Group of The Iron and Steel Institute). "*The Abbey Works of the Steel Company of Wales, Ltd.*," by W. F. Cartwright.

25th Jan.—(Joint Meeting with the Sheffield Section of the Institute of Metals). "*Cast Corrosion-Resisting Alloys*," by M. M. Hallett.

19th Feb.—"*Some Aspects of Modern Steelmaking*," by A. Robinson.

19th March—"*Accountancy as the Servant of Management*," by R. Peddie.

16th April—Film Night.

All Meetings will be held at the Royal Victoria Station Hotel, Sheffield, at 6.15 P.M., with the exception of the Joint Meeting on 25th January which will be held at the Grand Hotel, Sheffield, at 6.15 P.M.

NEWS OF SCIENCE AND INDUSTRY

Industrial Instrumentation and Automatic Process Control

A course of lectures on Industrial Instrumentation and Process Control is being held at Battersea Polytechnic, commencing on 16th October, 1950. The course is divided into nine series as follows :

A. The Principles of Automatic Process Control (16th, 23rd, 30th October, and 6th November, 1950)
B. Recorders and Controllers (13th, 20th, 27th November, and 4th, 11th December, 1950)
C. Motorised Control Valves and Positioners (13th, 22nd January, 1951)
D. Temperature Measurement and Control (29th January, 5th, 12th, 19th, 26th February, and 5th March, 1951)
E. Level Measurement and Control (12th, 19th March, 1951)
F. Flow and Flow Ratio Control (7th, 14th, 21st, 28th May, and 4th June, 1951)
G. Pressure Measurement and Control (11th, 18th June, 1951)
H. Telemetering (25th June, 2nd, 9th July, 1951)
I. The Principles of Transform Methods in Mathematics (3rd, 10th, 17th, 24th, 31st May, and 7th June, 1951).

The lectures will be held at 7 P.M. and time for discussion will be arranged ; each evening session will terminate at 9 P.M. Details of fees, etc., may be obtained from the Secretary, Battersea Polytechnic, London, S.W.11.

Third World Petroleum Congress

A Committee of Honour is now being formed in connection with the Third World Petroleum Congress, to be held from 28th May to 6th June, 1951. The formal opening session will be held in the Netherlands Ridderzaal (Hall of Knights) in The Hague.

International Congress on Analytical Chemistry, 1952

An International Congress on Analytical Chemistry is to be held at Oxford, commencing on 4th September, 1952. Accommodation will normally be provided in the colleges, but some hotel accommodation will also be available. The technical sessions will be held in one of the main University buildings.

The period of the Congress will include a week-end, and excursions and visits will be planned to take place during this period.

Beilby Memorial Awards

From the interest derived from the invested capital of the Sir George Beilby Memorial Fund, at intervals to be determined by the administrators representing the Royal Institute of Chemistry, the Society of Chemical Industry, and the Institute of Metals, awards are made to British investigators in science to mark appreciation of records of distinguished work. Preference is given to investigations relating to the special interests of Sir George Beilby, including problems connected with fuel economy, chemical engineering, and metallurgy, and awards are made, not on the result of any competition, but in recognition of continuous work of exceptional merit, bearing evidence of distinct advancement in science and practice.

In general, awards are not applicable to workers of established repute, but are granted as an encouragement to younger men who have done original independent work of exceptional merit over a period of years.

More than one award may be made in a given year if work of sufficient merit by several candidates is brought to notice. In 1949 three awards, each of 100 guineas, were made to Mr. F. R. N. Nabarro, Dr. C. E. Ransley, and Dr. K. W. Sykes respectively.

Consideration will be given to the making of an award or awards from the Fund early in 1951 and the administrators will therefore be glad to have their attention drawn to outstanding work of the nature indicated, not later than 31st December, 1950.

All communications on this subject should be addressed to the Convener of the Administrators, Sir George Beilby Memorial Fund, Royal Institute of Chemistry, 30 Russell Square, London, W.C.1.

Society of Instrument Technology

With the March 1950 issue, the *Transactions* of the Society of Instrument Technology have been published quarterly. The papers published in the *Transactions* represent the more important papers presented and discussed at the monthly meetings of the Society in London and at the local centres, and cover all aspects of instrument technology including the design, application, and maintenance of instruments.

Rapid development, accelerated by the need for extreme speed in gunnery, radar, and special requirements of new industrial processes, has been made in automatic control mechanisms, and the Society has now formed a Control Section entirely devoted to encouraging progress in this subject.

The Ministry of Supply Panel on Servo-mechanisms, formed in 1942 as an informal body for the exchange of information, had not the necessary status to co-ordinate Service requirements and make recommendations for the allocation of research and development facilitites, and was therefore later replaced by the Inter-departmental Committee. The activities of this Committee, however, do not include a forum where the scientific, technical, and educational sides of such control mechanisms can be freely discussed. To fulfil this need the Control Section, which should appeal to all interested in the control field, has been formed. The Section is intended to cover the theory and practice of closed-loop control systems, including servo-mechanisms, regulators, and press controllers, and problems of the human operator as controller, and when part of a larger control system.

British and American Liaison in Steel Castings Research

It has been announced that a basis of collaboration has been established between the Technical and Research Division of the Steel Founder's Society of America and the Research and Development Division of the British Steel Founders' Association.

It is understood that these two research organizations —which have been formed and are strongly supported

by the steel foundry industries in the U.S.A. and in the United Kingdom respectively—will exchange information relating to their research programmes and upon certain specified fields of research, both fundamental and applied.

CORRIGENDA

Studies in the Deoxidation of Iron: Deoxidation by Aluminium

The following corrections should be made to the paper by H. A. Sloman and E. L. Evans, published in the May, 1950, issue of the *Journal* (vol. 165, pp. 81–90):

Page 86, left-hand column, 13 lines from bottom, for "lower" read "upper" and 11 lines from bottom, for $1{\cdot}6 \times 10^{-12}$ read $2{\cdot}2 \times 10^{-10}$.

Page 86, right-hand column, line 4 should read:

$$\text{Log}K = -\frac{58{,}600}{T} - 20{\cdot}86 \pm 2$$

and lines 7 and 8 should read:

Kubaschewski: $\log K = -13{\cdot}5, -12{\cdot}4$
Geller and Dicke: $\log K = -11{\cdot}7, -10{\cdot}4$

The Use of the Oxygen Lance in British Electric Furnace Practice

The following corrections should be made to the paper by T. H. Harris, D. J. O. Brandt, and W. H. Everard, published in the August, 1950, issue of the *Journal* (vol. 165, pp. 399–418):

Page 407, right-hand column, fourth paragraph, first line, should read "Five special 26-ton heat. . . ."

Page 408, Table V, the heading should read "26-Ton Heats" and the column headed "Oxygen to Remove Phosphorus, lb." should read "Oxygen to Remove Phosphorus, %."

Effect of Cold-Work on Steel

The following corrections should be made to the papers by J. H. Andrew and H. Lee and others published in the June, 1950, issue of the *Journal* (vol. 165, pp. 145–184) and in the August, 1950, issue (vol. 165, pp. 369–395):

June issue, p. 179, 2nd term on right-hand side of equation (6) should be

$$\frac{\Delta l}{l}$$

August issue, p. 372, Fig. 44(*a*), the units of strain should read in hundredths, *i.e.*, $-0{\cdot}04$ etc.

Penetration of Molten Metal into Compacted Sand

The following corrections should be made to the paper by T. P. Hoar and D. V. Atterton, published in the September, 1950, issue of the *Journal* (vol. 166, pp. 1–77):

Fig. 7 (plate), (*a*) and (*b*) should be transposed.

DIARY

2nd Nov.—LIVERPOOL METALLURGICAL SOCIETY (Joint Meeting with the Liverpool and District Branch of the Institute of Welding)—"*Recent Work of the British Welding Research Association*," by H. G. Taylor—Lecture Theatre, Electricity Service Centre, Whitechapel, Liverpool, 7.0 P.M.

3rd Nov.—MANCHESTER ASSOCIATION OF ENGINEERS—"*Modern Heat-Treatment Furnaces*," by L. G. A. Leonard—The Engineers' Club, 17 Albert Square, Manchester, 6.45 P.M.

7th Nov.—SHEFFIELD METALLURGICAL ASSOCIATION—"*The Determination of Tantalum and Niobium in Highly Alloyed Steels*," by A. R. Powell—Grand Hotel, Sheffield, 7.0 P.M.

14th Nov.—SHEFFIELD METALLURGICAL ASSOCIATION—"*Geology in the Service of Iron and Steel*," by W. Davies—Grand Hotel, Sheffield, 7.0 P.M.

15th–16th Nov.—IRON AND STEEL INSTITUTE—Autumn General Meeting—4 Grosvenor Gardens, London, S.W.1, 10 A.M.

15th–16th Nov.—INSTITUTION OF ELECTRICAL ENGINEERS (Utilization Section)—Conference on "*Electricity as an Aid to Productivity*"—Savoy Place, W.C.2, 9.30 A.M.

17th Nov.—WEST OF SCOTLAND IRON AND STEEL INSTITUTE—"*The Welding of Pressure Vessels*," by H. Harris—39 Elmbank Crescent, Glasgow, 6.45 P.M.

17th Nov.—MANCHESTER ASSOCIATION OF ENGINEERS—"*The Use of Mechanical Stokers and Coal Handling Plant for Industrial Boiler Houses*," by R. W. F. Guy and J. P. Lauder—The Engineers' Club, 17 Albert Square, Manchester, 6.45 P.M.

20th Nov.—SHEFFIELD SOCIETY OF ENGINEERS AND METALLURGISTS—"*The Scope and Aims of the Sheffield University Post-Graduate School in Physical Metallurgy*," by A. G. Quarrell—Royal Victoria Station Hotel, Sheffield, 6.15 P.M.

21st Nov.—SHEFFIELD METALLURGICAL ASSOCIATION (Joint Meeting with The Iron and Steel Institute)—"*The Overheating of Steel*," by Professor A. Preece—Grand Hotel, Sheffield, 7.0 P.M.

22nd Nov.—INSTITUTE OF BRITISH FOUNDRYMEN (London Branch)—Discussion on "*Repair and Reclamation of Castings*," by A. B. Everest and R. W. Ruddle—Waldorf Hotel, Aldwych, W.C.2, 7.30 P.M.

22nd Nov.–2nd Dec.—NATIONAL SMOKE ABATEMENT SOCIETY—Fuel Efficiency in Industry and Home Exhibition—City Hall, Manchester.

28th Nov.—SHEFFIELD METALLURGICAL ASSOCIATION (Joint Meeting with the Royal Institute of Chemistry)—"*A Survey of the Physical Chemistry of Sulphur in Steelmaking*," by C. E. A. Shanahan—Grand Hotel, Sheffield, 7.0 P.M.

30th Nov.—INSTITUTION OF ELECTRICAL INSPECTION—"*Non-Destructive Testing in Steelworks Inspection*," by J. F. Hinsley—Royal Society of Arts, John Adam Street, Adelphi, W.C.2, 6.0 P.M.

TRANSLATION SERVICE

(The previous announcement was made in the October, 1950, issue of the *Journal*, p. 153.)

TRANSLATIONS AVAILABLE

No. 409 (Russian). A. P. BELOPOL'SKIY and S. YA. SHPUNT: "The System $FeSO_4$–H_2SO_4–H_2O at 50–90° C." (*Journal of Applied Chemistry (Russia)*, 1941, vol. 14, No. 6, pp. 716–733).

No. 410 (Hungarian). I. SAJÓ: "Rapid Analysis of Open-Hearth and Blast-Furnace Slags." (*Bányászati és Kohaszati Lapok*, 1950, vol. 5, Jan., pp. 68–70).

TRANSLATIONS IN COURSE OF PREPARATION

(German). W. KOCH: "Electrolytic Isolation of the Carbides in Alloyed and Unalloyed Steels." (*Stahl und Eisen*, 1949, vol. 69, Jan. 6, pp. 1–8).

(German). F. WEVER and W. KOCH: "The Transformation Kinetics of Steels. The Compositions of the Reactants during the Transformation of a Chromium–Manganese Steel in the Pearlite Range." (*Archiv für das Eisenhüttenwesen*, 1950, vol. 21, May/June, pp. 143–152). (Translated by Mr. C. B. Lander and made available through the courtesy of the Development and Research Department of The Mond Nickel Co., Ltd., Birmingham).

ABSTRACTS OF CURRENT LITERATURE *and* BOOK NOTICES

IRON AND STEEL MANUFACTURE AND RELATED SUBJECTS

CONTENTS

	PAGE
Fuel—Preparation, Properties, and Uses	257
Temperature Measurement and Control	257
Blast-Furnace Practice and Production of Pig Iron	258
Treatment and Use of Slag	259
Production of Steel	259
Foundry Practice	260
Heat-Treatment and Heat-Treatment Furnaces	263
Forging, Stamping, Drawing, and Pressing	264
Rolling-Mill Practice	264
Machinery for Iron and Steel Plant	264
Welding and Flame-Cutting	265
Cleaning and Pickling	267
Protective Coatings	267
Properties and Tests	268
Metallography	269
Corrosion	270
Analysis	271
Miscellaneous	271
Book Notices	271
New Publications	272

FUEL—PREPARATION, PROPERTIES, AND USES

Industrial Gas Combustion with Oxygenated Air. (Steel, 1949, vol. 125, Nov. 14, pp. 96, 98). The Surface Combustion Corp., Toledo, O., at the instance of the American Gas Association, has carried out work on the effect of oxygen-enriched air on the combustion of industrial gas. Among advantages cited are the higher temperatures obtainable and a financial economy even at low temperatures. Problems still to be solved include the design of burners and control gear, and the development of new refractories.—J. P. S.

Development and Possibilities of Improvement in the Heat Economy of Iron and Steel Works. F. Wesemann. (Stahl und Eisen, 1950, vol. 70, Jan. 5, pp. 1–10). An exhaustive survey is made of the relation between the specific heat consumption and various process data, especially the degree of activity, in respect of integrated iron and steel works, a works producing and rolling steel, and an independent rolling mill. Desirable specific heat consumptions are derived from general thermal considerations and optimum process data. It is shown, in general, that a comparison of the nominal with the actual consumption data points the way to important economies to achieve which does not require extensive new equipment and alterations, but attention to details of the existing plant.—R. A. R.

Checking Tests for the Cleaning of Coal. R. Cheradame, P. L. R. Saint Guilhem, A. Raineau, and P. Belugou. (Colliery Guardian, 1950, vol. 180, Feb. 23, pp. 240–242). The author describes methods of presenting and comparing the results obtained in tests on the efficiency of coal cleaning by different plants at French collieries ; these consisted of 14 fixed-screen jigs, one heavy-liquid trough, three rheolaveur coal-cleaning units, and two pneumatic tables.—R. A. R.

Temperature Control for Coke Ovens. H. Cassan. (Chaleur et Industrie, 1950, vol. 31, Mar., pp. 76–78). Owing to the difference in internal width between the ends of modern coke ovens, it is the common practice to graduate the temperature of the burners along the oven so that there exists a 50° C. average difference between the burners at each end. The author discusses the mathematics of this practice and suggests that this 50° C. difference is too small, resulting in the charge at the pusher end being overcoked. Economies in fuel may be achieved either by increasing the graduated differences in temperature of the individual burners, or by increasing the rate of charge. Practical tests should be made to confirm this theory and find the optimum temperatures.—R. F. F.

The Pressure Drop and Change of State in Long-Distance Gas and Steam Lines. H. Baer. (Forschung auf dem Gebiete des Ingenieurwesens, B, 1949–50, vol. 16, No. 3, pp. 79–84). The changes in pressure, volume, and velocity of gases in long horizontal pipelines of constant diameter are calculated. A graphical method, using the Mollier diagram, for calculating the heat lost by steam is explained ; it takes into account the change in the coefficient of friction in relation to the Reynolds number along the pipeline.—R. A. B.

TEMPERATURE MEASUREMENT AND CONTROL

Optical Temperature Scale and Emissivity of Liquid Iron. M. N. Dastur and N. A. Gokcen. (Transactions of the American Institute of Mining and Metallurgical Engineers, 1949, vol. 185, pp. 665–667 : Journal of Metals, 1949, vol. 1, Oct.). Optical measurements of the temperature of liquid iron were carried out in an induction furnace. Two sets of simultaneous temperature readings were obtained : (1) Top temperature reading by a sensitive optical pyrometer, and bottom reading from a thermocouple touching the top of the crucible cavity. (2) Top and bottom optical temperature readings by using the crucible cavity as a perfect black body for the bottom pyrometer. The results are plotted. The emissivity of liquid iron was calculated from observed top temperatures by the Wien-Planck equation using the true and observed temperatures obtained. The total change in the emissivity of liquid iron over the temperature range of 1540–1900° C. is from 0·42 to 0·50. The result of this investigation is presented graphically with the results obtained by previous investigators showing the inconsistency of the reported emissivity values.—R. E.

Temperature Measurement in Basic Arc Furnace. C. B. Post and D. G. Schoffstall. (Journal of Metals, 1949, vol. 1, Oct., pp. 12–17). The authors describe a modified immersion Rayotube and its use for measuring bath temperatures in the basic electric furnace. The instrument is simple in application and requires no skilled personnel in operation. Any number of readings can be taken during the course of a heat with reproducible results. At the plant of the Carpenter Steel Co., Reading, Pa., where the instrument is in use, dry nitrogen is used instead of air, and the amount consumed on each reading is about 70 cu. ft.—R. E.

Method for Determining the Temperature of the Melt in the Blowing Converter. G. Naeser and W. Pepperhoff. (Stahl und Eisen, 1950, vol. 70, Jan. 5, pp. 22–24). After reviewing attempts which have been made to measure the temperature of molten steel in the converter a new method is described. The radiation from the metal through a tuyere in the converter bottom is measured by two photocells of different spectral sensitivity. The temperature is determined from the ratio of the intensities and recorded by an electronic instrument. Time–temperature curves for two blows are presented ; they show a rise in temperature during blowing from 1200° to 1700° C.—R. A. R.

Temperature and Flame Measurements in the Bessemer Process. G. Gille and J. Willems. (Iron and Steel Institute, 1950, Translation Series, No. 402). This is an English translation of a paper which appeared in Stahl und Eisen, 1949, vol. 69, Oct. 27, pp. 759–762 (*see* Journ. I. and S.I., 1950, vol. 165, May, p. 105).—R. A. R.

Bath Temperature Measurements. J. G. Mravec. (Blast Furnace and Steel Plant, 1949, vol. 37, Dec., pp. 1447–1450). The advantages and disadvantages of the immersed thermocouple and the blowing tube radiation pyrometer are discussed. Use of the former appears to be increasing ; it is favoured for its accuracy, dependability, and ease of handling.—J. P. S.

Temperature Measurement in Heat-Treating and Reheating Furnaces. (Boletin Minero e Industrial, 1949, vol. 28, Dec., pp. 583–586). [In Spanish]. The thermoelectric pyrometer discovered by Seebeck in 1821, is described. The applications of well-known types of thermocouple are stated. The author then examines the characteristics and uses of compensation circuits, millivoltmeters, and optical and total radiation pyrometers.—R. S.

Contribution to the Study of Variable Operating Conditions in Furnaces. Heating of an Uncharged Furnace at Constant Pressure. An Experimental Study on a Semi-Industrial Scale. V. Broïde and C. Henry. (Chaleur et Industrie, 1949, vol. 30, Aug., pp. 181–186 ; Sept., pp. 207–223 ; Oct., pp. 239–248). Continuing a programme of research work on operating conditions in furnaces (*see* Journ. I. and S.I., 1948, vol. 159, May, p. 90) the authors have studied experimentally the increase in temperature–time relationship in a semi-industrial uncharged electric furnace heated at constant calorific pressure starting at room temperature. Formulæ are derived and methods are proposed for calculating furnace conditions which can be extended to the case of a charged furnace.—J. C. R.

BLAST-FURNACE PRACTICE AND PRODUCTION OF PIG IRON

Electrical Equipment and Distribution for the Blast Furnace Plant. C. P. Hamilton. (Blast Furnace and Steel Plant, 1949, vol. 37, Nov., pp. 1339, 1340, 1358). The electrical load for blast-furnace operation and its distribution are discussed, and recommendations are made on the selection of components for the skip-hoist drive.—R. A. R.

Contribution to the Study of the Use of Cowper Stoves in Siderurgy. G. Namy. (Centre de Documentation Sidérurgique, Circulaire d'Informations Techniques, 1949, vol. 6, Mar., pp. 121–140). A detailed report is submitted on the use and efficiency of Cowper stoves in blast-furnace practice. J. C. R.

The Checkerwork of the Modern Cowper Stove. M. Gérin. (Société Française de Métallurgie, Oct. 3, 1949 : Revue de Métallurgie, Mémoires, 1950, vol. 47, Apr., pp. 295–304). After discussing the conditions in which the checkerwork of a Cowper stove has to work, the most suitable characteristics of good checkerwork, and present-day designs, the author describes his own design in which he aims to match the weight of refractory to the intensity of heat exchange in each zone and to achieve maximum thermal utilization of the whole mass of the refractory material without risk of obstruction or of unnecessary pressure loss. He presents a theoretical thermal comparison of a checkerwork of the classic type with one of the Gérin type, and also some results obtained on a stove which only partially conformed to his ideas. In conclusion he discusses a few criticisms that may be levelled at his design, and comments on turbulence as a factor in the improvement of heat exchange and the Cowper stove as a heat accumulator.—A. E. C.

Cowper Stoves in French Siderurgical Industry. V. Rémond. (Société Française de Métallurgie, Oct. 3, 1949 : Revue de Métallurgie, Mémoires, 1950, vol. 47, May, pp. 365–387). In the first chapter a large table gives details of the various Cowper stoves in operation in French works during 1948–1949, and these are then discussed under the headings of types of checkerwork, quality of the bricks, construction, heating of the stoves, control, and operation. The various patented types of checkerwork in use are illustrated and described (Hotspur, Kennedy-Brassart, Brohltal, Martin and Pagenstecher, Schiffert and Kircher, Steuler, Labesse, and Daniel Petit). The thermal balance of the Cowper stove, the temperature conditions to which the refractories are exposed, the properties required in the materials, and the accumulation of heat in the stove all receive attention.—A. E. C.

Mary Blast Furnace—Last of Hand-Filled Stacks in America. J. D. Knox. (Steel, 1949, vol. 125, Oct. 10, pp. 136–144). The Mary blast-furnace at Lowellville, O., was erected as a stone stack in 1846, especially to operate on raw coal, a local bituminous splint coal being used ; the ore was a Lower Coal Measure carbonate ore, mixed with Lake Superior ore and rolling-mill cinder. Known originally as the Mahoning stack, it was rebuilt in 1872, 56 ft. high, with an iron shell, and rechristened Ada ; its capacity was now 8000 tons of iron per year, and Lake Superior ores were then being smelted with coke and coal mixed. Charging was, of course, by hand, a water-powered elevator lifting the materials to the charging platform. Between this time and 1880 when the name was changed to Mary, hot-blast stoves were installed. Its capacity was thus raised to about 90 tons/week. Later improvements, including new stoves, and a new blowing engine increased this to 60,000 tons/year by 1890. In 1914–15, the owners at that time erected a steelworks for which ' Mary ' supplied 350 tons of iron a day ; by then its height was 85 ft., with a hearth diameter of 18 ft. Today, the furnace, now 81 ft. high with a 13 ft. 6 in. hearth, is still hand-filled ; though mechanical power is used to bring the charges to the elevator, the filled barrows are tipped on to the charging bell by an operator known as the top-filler. The rated capacity of the furnace is still 350 tons/day, but this is exceeded in practice. Steam blowing engines nearly 50 years old are still in use. This is the last hand-filled blast-furnace operating in the United States.—J. P. S.

Extra Coke *vs.* Burden Cut. K. Neustaeder. (Blast Furnace and Steel Plant, 1949, vol. 37, Dec., pp. 1443–1446). This article deals with the two methods of varying the ore/coke ratio in the blast-furnace to allow for minor changes in working—(1) the ' extra coke ' method, that of charging additional coke at regular or irregular intervals ; (2) the ' burden cut ' method, that of increasing or decreasing the ore charge while keeping the coke charge constant. The effects of both procedures are described and considered, but no clear preference is expressed.—J. P. S.

Note on the Use of Quicklime in the Blast Furnace Charge. Logelin. (Centre de Documentation Sidérurgique, Circulaire d'Informations Techniques, 1949, vol. 6, Mar., pp. 102–103). The effects of adding quicklime to the blast-furnace charge are briefly discussed. A note is included on tests carried out by the Société Métallurgique de Normandie.—J. C. R.

Effect of Coke Stability on Operation of Blast Furnaces. J. F. Peters. (American Institute of Mining and Metallurgical Engineers, Blast Furnace, Coke Oven and Raw Materials Conference, 1949, Proceedings, vol. 8, pp. 7–31). An investigation of the effect of the ability of coke to withstand crushing in blast-furnace operation is reported. This resistance to crushing was measured by the amount of breeze produced by normal handling between the arrival wharf and the skip hoist on the furnace. Many curves are presented which show that the amount of breeze formed during coking of the coal and transport of the coke is a good index of furnace production. Charts also show the close correlation between the amount of breeze and the maximum wind rate, coke consumption, volatile matter in the coke, tumbler test data, and gas flow at the periphery of the furnace.—R. A. R.

Distinctions between Large and Small Blast Furnaces at the Inland Steel Company. T. F. Plimpton. (American Institute of Mining and Metallurgical Engineers, Blast Furnace, Coke Oven and Raw Materials Conference, 1949, Proceedings, vol. 8, pp. 101–107). Data on the production of iron in large and small blast-furnaces are presented and the economics of production are compared. The eight furnaces in question have hearth diameters of 17 ft. 3 in., 19 ft., 20 ft. (two furnaces), and 25 ft. 9 in. (four furnaces). The rated production per day in short tons of the furnaces is calculated by multiplying the area of an annular ring (outer dia. = hearth dia., inner dia. = hearth dia. — 3 ft. 6 in.) by a factor of 4·74. In general, the cost of production is less the larger the furnace, but larger furnaces suffer more from weak coke than the smaller furnaces.—R. A. R.

Some Aspects of Operation of Large and Small Blast Furnaces. G. P. Burks. (American Institute of Mining and Metallurgical Engineers, Blast Furnace, Coke Oven and Raw Materials Conference, 1949, Proceedings, vol. 8, pp. 107–115).

Data on size, shape, operation, and production relating to 12 blast-furnaces, five with hearths 20 ft. 6 in., four with hearths 25 ft. 6 in., and one with a hearth 26 ft. 6 in. in dia. are presented and discussed. A comparison of the data indicates that the production of iron per unit of hearth of the large furnaces will approach that of the small furnaces when high-grade raw materials are available to both. If the quality of raw materials deteriorates, the small furnaces will maintain a proportionately higher rate of production than the large furnaces. The relation between the coke rates for the large and small furnaces remains the same while both rates increase owing to the deteriorating quality of the raw materials. The silicon content of the iron produced in the large furnaces is more uniform.—R. A. R.

Operating Data on Small Furnaces *versus* Large Furnaces. J. K. Dye. (American Institute of Mining and Metallurgical Engineers, Blast Furnace, Coke Oven and Raw Materials Conference, 1949, Proceedings, vol. 8, pp. 116–120). Operating data for three blast-furnaces with hearths 13 ft. 9 in., 14 ft. 6 in., and 25 ft. 9 in. in dia. at Ashland, Kentucky, are compared. The chemical composition of the iron, in particular the silicon content, is more easily controlled with a small than a large furnace, and there is less difficulty when taking the small furnaces off wind. Data on the replacement of copper fittings (tuyeres, slag notches, and coolers) indicate that the loss of copper increases directly with the furnace size.—R. A. R.

Operating Data on Small and Large Blast Furnaces. C. F. Hoffman. (American Institute of Mining and Metallurgical Engineers, Blast Furnace, Coke Oven and Raw Materials Conference, 1949, Proceedings, vol. 8, pp. 121–131). Data on the operation of two blast-furnaces (hearth diameters of 19 ft. and 28 ft.) for a period of one month when using the same ore, coke, and limestone, are compared and indicate that the large furnace gave better results with regard to quality of product, coke rate, and production rate.—R. A. R.

Application of High Top Pressure to the Blast-Furnace. H. Biers. (Instituto del Hierro y del Acero, 1949, vol. 2, Oct.–Dec., pp. 16–35). [In Spanish]. The author reviewed the practical advances and actual data obtained by the application of high top pressure to blast-furnaces over a period of two and a half years. A 30% increase in output, a 10 to 15% decrease in coke consumption, and a 50% decrease in flue dust were achieved. After outlining the limitations of the blast-furnace, the author described the pressurizing process and summarized the results. Graphs are given, showing the data obtained on the Youngstown furnaces. Coke consumption, production of flue dust, time lost, and quality of iron, are discussed in relation to high top pressure, and, finally, the economic aspects are reviewed.

The author concludes that the application of high top pressure to blast-furnaces constitutes a rapid and simple method of increasing the efficiency of the reduction of iron oxides in the blast-furnace. Coupled with the beneficiation of iron ore and the use of oxygen, it introduces a new flexibility into blast-furnace practice.—R. S.

15-Minute Pig Iron. (Journal of Metals, 1949, vol. 1, Sept., p. 24). A small electric steelmaking plant with a capacity of 500 lb./hr. in which ore briquettes are reduced in an electric furnace, is described. *See* Journ. I. and S.I., 1949, vol. 163, Oct., p. 221.

TREATMENT AND USE OF SLAG

Decomposition of Rock Phosphate in Liquid Blast-Furnace Slag. W. Wolf. (Stahl und Eisen, 1950, vol. 70, Jan. 5, pp. 24–26 : Génie Civil, 1950, vol. 127, July 1, pp. 253–254). In order to increase the amount of phosphorus in soluble form in blast-furnace slag fertilizers, attempts were made to get crude phosphate to decompose in the molten slag. A successful method was developed in which fine crude phosphate was blown by compressed air into a ladle full of molten slag.
R. A. R.

Investigations on Granulated Blastfurnace Slags for the Manufacture of Portland Blastfurnace Cement. T. W. Parker and R. W. Nurse. (Department of Scientific and Industrial Research, 1949, National Building Studies, Technical Paper No. 3 : H.M. Stationery Office). Samples of granulated slag have been incorporated into experimental Portland blast-furnace cements. All the slags tested had considerable hydraulic value and most of the experimental cement satisfied British Standard 146. Although, in general, hematite slags gave the best results, there was considerable overlapping with the basic and foundry-iron slags. The early strength was considerably affected by the ratio of gypsum to clinker and by impurities such as chlorides introduced into the slag. The general theory of the formation of hydraulic glasses is also discussed.—R. A. R.

PRODUCTION OF STEEL

The Use of Oxygen-Enriched Blast in the Basic Converter. Tests Carried Out at the Forges de la Providence at Rehon. (18 November 1947–30 December 1947). Cornet. (Centre de Documentation Sidérurgique, Circulaire d'Informations Techniques, 1949, vol. 6, Apr.–May, pp. 185–209). A detailed report is presented of tests with oxygen-enriched blast in the basic converter carried out by the Forges de la Providence at Rehon, France, to examine the effect of oxygen-enrichment on the melting of cold iron, the nitrogen content and the quality of the final product, the blowing period, and the proportion of scrap that can be incorporated in the charge. The blast was enriched in different tests during silicon elimination, during silicon and carbon elimination, and during silicon, carbon, and phosphorus elimination. Best results were obtained when the enriched blast was introduced during silicon and carbon elimination and cut off at the beginning of the phosphorus elimination stage. Extensive test data are presented in tabular form. In an appendix the practical application of this process at the Rehon works is discussed.
J. C. R.

Observations of the Course of the Reaction towards the End of the Bessemer Blow with the Aid of Temperature and Flame Measurements. J. Willems, G. Gille, and H. Höfges. (Iron and Steel Institute, 1950, Translation Series, No. 403). This is an English translation of a paper which appeared in Stahl und Eisen, 1949, vol. 69, Oct. 27, pp. 762–764 (*see* Journ. I. and S.I., 1950, vol. 165, May, p. 107).—R. A. R.

A New Procedure for Killing Steel in the Acid Converter. H. Laplanche. (Métallurgie, 1949, vol. 81, Dec., pp. 9, 11, 13). A modification of the acid-Bessemer process is suggested which, it is claimed, results in the final product having a homogeneous structure. After the blowing stage is over, liquid iron is added to the converter and the carbon in the iron eliminates the oxygen in the steel as a gas. Ferro-manganese and ferrosilicon are added either in the converter or in the ladle. Finally deoxidation is completed by the addition of 0·10–0·15% of aluminium to the ladle.—J. C. R.

A Study of an Open Hearth Combustion System. M. Sample. (Blast Furnace and Steel Plant, 1949, vol. 37, Nov., pp. 1327–1334). A report is presented of research work on combustion in an oil-fired open-hearth furnace with the object of providing better control of air for combustion, improving regulation of the draught, providing practical instrumentation to guide the first helper, and improving the control of reversals and of steam for atomizing. The results included the following : (1) A close control of the air supplied for combustion is needed ; (2) air for combustion should be corrected or compensated for the ambient air temperature ; (3) a sensitive pressure recorder should be fitted and used to maintain a close balance between the draughts at the incoming and outgoing ends ; (4) furnace pressure should not exceed 0·030 in. of water at the crown of the arch ; (5) excess air should be kept at a minimum—at 3·5% oxygen for the furnace studied ; and (6) mixing throats should be designed to direct the air for combustion on the oil stream.—R. A. R

Furnace Bottom Installed in 57 Hours in World's Largest Open-Hearth. H. N. Barrett. (Steel, 1949, vol. 125, Nov. 28, pp. 56–58). Brief particulars are given of the bottom of a new 550-ton open-hearth furnace at the works of the Weirton Steel Company. This hearth was lined with Ramset, a magnesia clinker designed to resist hydration, to form a rammed monolithic covering 13 in. thick at the bottom and 15 in. thick at the sides. The finished measurements were 18 ft. × 58 ft. at sill level ; the bath depth at the taphole is 45 in.—R. A. R.

Blowing High-Chromium Melts with Pure Oxygen in the Arc Furnace. R. Fischer. (Stahl und Eisen, 1950, vol. 70, Jan. 5, pp. 10–21). Trials were run with a 7½-ton arc furnace to determine the recovery of alloying elements when working charges of 100% high-alloy chromium-nickel steel scrap.

By blowing commercially pure oxygen into the bath below the slag level the carbon could be reduced to 0·04% at a rate of 0·84%/hr. The amount of oxygen consumed per kilogramme of carbon was several times the amount given in the literature for plain carbon steels and it varied greatly with the initial carbon content, the degree of decarburization, and the proportion taken up by the other elements, *e.g.*, silicon, aluminium, and titanium. The high temperature necessary for the process shortened the life of the lining. The properties of the steel produced were in no way inferior to those of steel of the same composition prepared without oxygen blowing. Trials with chromium-bearing scrap high in silicon, and high in manganese are also reported. No data on the economic aspect are given, but the general conclusion is that the savings in time and current approximately balance the cost of oxygen, steel tubing, and lining wear, so that there remains a considerable gain by the increased use of the highly alloyed scrap.—R. A. R.

Oxygen Injection Process in Melting Low Carbon Cr–Ni Stainless Steel. H. J. Cooper. (American Foundryman, 1949, vol. 16, Aug., pp. 44–46). Experiments were carried out in acid-lined direct arc furnaces to determine the effect of the use of oxygen in melting low-carbon chromium–nickel stainless steel. Data obtained showed that best results were obtained when oxygen was injected when the bath temperature was about 3000° F. Results indicated that although considerable furnace time could be saved by injecting oxygen during or immediately after melting down, the chromium loss was greater than that which occurred if the oxygen injection was delayed until later. Some of the economies effected by this method are discussed.—J. C. R.

Decarburization in the Basic Arc Furnace. Achard. (Centre de Documentation Sidérurgique, Circulaire d'Informations Techniques, 1949, vol. 6, Feb., pp. 71–82). A report is presented on the author's investigations on decarburization in the basic arc furnace. After analyzing decarburization factors, such as carbon and manganese contents, and their influence on the structure of the steel, he discusses the theory of decarburization and presents the data obtained on the speed of decarburization from his tests. He suggests that to obtain best quality steel, carbon over 0·3% should be eliminated, the speed of decarburization should not exceed 0·005%/min., and decarburization should stop before the carbon content falls below 0·1%.—J. C. R.

Production of Stainless Steel. B. H. DeLong. (Steel, 1949, vol. 125, Oct. 31, pp. 64–73; Nov. 7, pp. 132–140; Nov. 14, pp. 102–115). The author begins his study of stainless steel by describing its early history, and then passes on to present-day manufacture in the basic arc furnace and the high-frequency induction furnace; he deals next with casting practice, reheating and cogging, and stresses the necessity for surface grinding and pickling, especially before wire-drawing and sheet-rolling. In the second part he deals with types of corrosion encountered in service, intergranular corrosion, galvanic corrosion and pitting corrosion, and describes tests, *e.g.*, the copper sulphate test, the boiling nitric acid and salt-spray tests which may be used to determine the corrosion-resisting properties of a given stainless steel. He provides tables, one giving the American Iron and Steel Institute classification of stainless steels and another displaying the chemical analyses, working properties, corrosion resistance, etc., of the three groups, martensitic, ferritic, and austenitic stainless steels. In the third part he goes on to discuss these in greater detail, with reference to the A.I.S.I. classification numbers, and concludes with some discussion of fabricating processes, including the development of free-cutting stainless steels, the advantages of niobium- and titanium-containing welding qualities, and the use of hard and soft soldering.

FOUNDRY PRACTICE

Factors for Immediate Consideration in Assisting in the Future Production of Medium and Heavy Iron Castings. G. W. Nicholls. (Proceedings of the Institute of British Foundrymen, 1949, vol. 42, pp. B61–B74). The paper brings to the notice of designers and foundrymen factors relating to casting design, pattern construction, contraction, shrinkage, metal composition, runners, risers, cores, and casting procedure for medium and heavy castings, which will help the foundry to produce sound castings economically at the first attempt.—R. A. R.

Quality Control Review—Test Procedures for Quality Control of Gray Iron Castings. F. J. Walls. (American Foundryman, 1949, vol. 16, Nov., pp. 51–59). This review incorporates brief descriptions of many tests and procedures at all stages in the production of iron castings from the raw materials supplied to the cupola to inspection and testing of the finished castings.—R. A. R.

Increased Refractory Life in Malleable Melting. J. Henley. (American Foundryman, 1949, vol. 16, Dec., pp. 30–31). To prevent piling of the charge against the cupola wall on the side opposite to the charging opening a counterweighted swing door has been fitted to the charging skip, and the weight on the door is adjusted to ensure the charge falling in the centre, thus prolonging the lining life. A method of laying the bricks for the hearth of an air furnace to provide the slope to the taphole is described in detail.—R. A. R.

Maintenance of Air Compressors. G. B. Comfort. (American Foundrymen's Society: Foundry, 1949, vol. 77, Nov., pp. 78, 79, 190–192). Recommendations are made on the maintenance of air compressors, receivers, and pipeline in foundries. R. A. R.

Patching the Cupola—Develop Air-Placement Process. N. J. Dunbeck and T. E. Barlow. (American Foundryman, 1949, vol. 16, Oct., pp. 48–57). An account is given of extensive laboratory, pilot, and full-scale cupola tests for determining the optimum mixture of cupola patching material for application with a compressed-air gun. The percentage of clay may range from 15 to 25 if it is of the proper quality. A combination of rounded Ohio ganister, which is essentially plus 20 mesh and minus $\frac{5}{16}$ in. with either fine crushed ganister or fine pure silica sand with clay in the proportion 2 : 2 : 1 by volume gives best results. The coarse ganister should not exceed 60% of the mixture, the preferable amount being 42–50%. Silica flour might improve the quality of the lining but was unsuitable for application with the gun. This mixture is conveyed by compressed air to the gun where it is blended with water at the nozzle under control of the operator.

Standards Must Be Observed in Cupola Operations. R. H. Olmsted. (Foundry, 1949, vol. 77, Nov., pp. 78, 79, 200–204). An investigation of the causes of frequent burning out in certain areas of a cupola of 78 in. inside dia. is reported. The cupola had two slag holes at the back and the 'burn-outs' occurred in the area above them. It was found that by carefully blocking off small areas of the two tuyeres nearest the slag hole, having only one slag hole positioned at equal distances from the two nearest tuyeres, and making a slight change in the windbox arrangement, the 'burn-outs' became relatively small and the blast distribution was more uniform. R. A. R.

Develops New Type Unit for Desulphurizing Cupola Iron. F. E. Bates. (Foundry, 1949, vol. 77, Nov., pp. 88–91). A description is given of equipment for adding soda ash to the metal at the cupola spout and for dealing with the slag. The soda ash in granular form is fed down a tube from a hopper through one of several holes in a sliding plate, by which the rate is adjusted, into the metal entering the forehearth, the latter containing iron to a depth of about 12 in. with about 5 in. of slag on top. A slag runner leading to an opening in a 12-in. steel pipe, through which water flows rapidly, provides for the removal of the slag, and a teapot spout at the front of the forehearth delivers clean desulphurized metal to the ladles. Continuous and effective desulphurization is obtained by this means.—R. A. R.

Stop Metal Losses and Watch Costs Go Down. A. D. Barczak. (American Foundrymen, 1949, vol. 16, July, pp. 50–55). After emphasizing the importance of reducing metal losses in foundry practice the author surveys the likely sources of losses and ways of eliminating or diminishing them.—J. C. R.

Possibilities of Utilizing Pig Iron Produced Under a High-Alumina Slag. N. Hajtó and F. Varga. (Bányászati és Kohászati Lapok, 1949, vol. 4, Nov., pp. 483–489). [In Hungarian]. The melting for these experiments was carried out in a 600-mm. dia. cupola of 1·8 tons/hr. capacity. Charges of 200 kg. were used, 12% of which consisted of coke. The limestone addition was 35 wt.-% of the coke. The blast pressure was about 450 mm. H_2O. The tapping temperature was 1380–1410° C. Three specimens 30 mm. in dia. × 600 mm. long were cast from each melt, and bending,

tensile, and hardness tests were carried out. The cast iron containing 3·2–3·4% of carbon was of a basically pearlitic structure. The melts which did not contain steel scrap produced material of low tensile strength, although its hardness was not much less than that of the specimens with higher tensile strengths. No relation was observed between the proportion of bauxite pig iron in the melt and the mechanical properties of the specimens, but the mechanical properties showed rapid improvement with increasing percentages of steel scrap in the charge. The main advantage of the bauxite pig iron is its high carbon and low sulphur contents, permitting the use of high percentages of steel scrap in the charge, which also reduced the danger of piping and increased the liquidity and density of the melt. Even melts containing 50% steel scrap made good castings with sharp edges. There was practically no evolution of gas during solidification owing to the aluminium and the titanium content of the bauxite pig iron. It was found that this iron could be used for producing grey and malleable cast iron.—E. G.

The Effect of Various Elements upon the Form of Graphite in Cast Iron. I. Iitaka. (Bulletin of the Institute of Physical and Chemical Research, vol. 21, No. 5, pp. 454–467). [In Japanese].

Converting the Eutectic Graphite of Cast Iron to a Flake Graphite. I. Iitaka. (Bulletin of The Institute of Physical and Chemical Research, vol. 22, No. 6, pp. 571–576). [In Japanese].

Spheroidal-Graphite Cast Iron. W. W. Braidwood and A. D. Busby. (Nickel Bulletin, 1949, vol. 22, Aug.–Sept., pp. 126–130). The production of nodular grey iron castings by additions of magnesium to the iron is discussed. *See* Journ. I. and S.I., 1950, vol. 164, Apr., p. 489.

Variables in Producing Nodular Graphite Cast Iron by Magnesium Treatment. G. E. Holdeman and J. C. H. Stearns. (American Foundryman, 1949, vol. 16, Aug., pp. 36–41). The alloying efficiency of various magnesium alloys with iron is examined. Copper–magnesium and nickel–magnesium compositions in which the magnesium content does not exceed 30% have given best results both from the efficiency of the magnesium and the reactivity aspects. The amount of the composition required and the method of adding it to the iron in the ladle are discussed. Brief details are given of the properties and treatment of nodular irons.—J. C. R.

Symposium on Nodular Graphite Cast Iron. (Transactions of the American Foundrymen's Society, 1949, vol. 57, pp. 576–587). At this Symposium, sponsored jointly by the Gray Iron and Malleable Divisions of the A.F.S., D. J. Reese gave some details of the production and properties of nodular cast iron produced in the U.S.A., using the technique of magnesium inoculation. C. K. Donoho described trials which showed that cupola metal could be treated from ladle to ladle to give consistent properties, and that the metal could be held as long as 15 min. without loss of the effect of the inoculation. G. Vennerholm stated that a low-sulphur blast-furnace iron could be remelted in an electric furnace and treated with 50/50 magnesium–copper alloy to produce nodular cast iron. R. G. G. McElwee pointed out the need for good control of the melting practice.—R. A. R.

Graphitization of Gray Cast Iron by Heat Treatment. A. W. Silvester. (Transactions of the American Foundrymen's Society, 1949, vol. 57, pp. 51–65). Extensive tests were made to study factors affecting the graphitization of two cast irons with silicon contents of 1·93% and 2·68% respectively. There is a maximum decomposition rate for the combined carbon and the reaction $Fe_3C \rightarrow 3Fe + C$ proceeds to the right at an increasing rate until all the iron carbide is decomposed. The range of temperature over which the iron carbide readily decomposed was greater in high-silicon than in medium-silicon iron.—R. A. R.

Nodular Graphite in Cast Iron. N. Hajtó. (Bányászati és Kohászati Lapok, 1949, vol. 4, Oct., pp. 425–433). [In Hungarian]. The problem of producing nodular cast iron in Hungary is dealt with, and it is reported that laboratory tests have been successful. Difficulties were encountered in the production of the necessary magnesium alloy. The initial material for this was a copper–magnesium alloy (Mg 20%). About 4·4% of the magnesium burnt away during the process. Melting was carried out in a graphite crucible. The first test series were carried out with Bauxite-type pig iron (C 4·65%, Mn 0·88%, Si 1·01%, S 0·034%, P 0·091%). The silicon content was made up by adding 90% ferrosilicon. In the second series, melting was carried out under a slag layer and the pig iron used had the composition C 3·65%, Mn 0·86%, Si 3·18%, S 0·094%, P 0·62%. Copper–magnesium alloy corresponding to 0·78% of magnesium was added to the melt and, 1 min. after casting, 90% ferrosilicon (corresponding to 0·42% Si) was added. Tests on a production scale will follow.—E. G.

Magnesium Additions and Desulphurization of Cast Irons. J. E. Rehder. (American Foundryman, 1949, vol. 16, Sept., pp. 33–37). In making magnesium alloy additions to molten iron a proportion of the magnesium is consumed in the desulphurizing reactions depending on the sulphur content of the iron, and sufficient magnesium must be left for nucleation to produce nodular graphite. Data on the effect of the initial sulphur on the magnesium available for nucleation when making increasing additions of 50/50 magnesium–copper alloy, and on the cost of producing magnesium-treated iron are presented. The cost of desulphurizing with soda ash is about the same as for desulphurizing with magnesium while treating the iron to produce nodular graphite.—R. A. R.

Heat Transfer . . . A Foundryman's Tool. V. Paschkis. (American Foundrymen's Society, 1949, Preprint No. 43: American Foundryman, 1949, vol. 16, July, pp. 59–63). In the first part of this paper the elements of the theory of heat flow are explained. The second part studies foundry practice from the thermal viewpoint, while the third part uses the electric analogy method by means of a heat and mass flow analyser machine, to solve foundry heat problems.—J. C. R.

Quality Control Review . . . Summarize Test Procedures for Malleable Foundrymen. M. O. Booth. (American Foundryman, 1949, vol. 16, July, pp. 56–58). The various stages at which control tests can be carried out in malleable iron casting, are outlined. Checks can be made on the raw materials and scrap, the core materials, chemical analysis, and temperature of melting and casting. Test sprues can be fractured at intervals and it is important that proper furnace repairs should be made.—J. C. R.

Segregation in Small Steel Castings. H. F. Bishop. (Foundry, 1949, vol. 77, Nov., pp. 74–77, 139, 140; Dec., pp. 72–76, 154–156). Examples of small steel castings are described in which the carbon content of the steel close to a riser junction is much higher than elsewhere in the casting—in some cases nearly twice as much. An investigation of the causes of this in which castings 4 in. in dia. × 4 in. high with different sizes and shapes of riser were used is described. The explanation put forward is that dendrites of low-carbon iron solidify first at the bottom of the riser, the remaining liquid becoming higher in carbon and it is this liquid which finally feeds the casting during solidification.—R. A. R.

Correct Mould Design for Steel Castings. G. Schmidt. (Neue Giesserei, 1949, vol. 36, Dec., pp. 372–378). It is shown how the design of a steel casting can be influenced by pattern-making, moulding, pouring, fettling and annealing, and machining considerations. Examples are described to show how initial designs can be improved from some of these points of view.—R. A. R.

Steel Castings in Welded Assemblies. J. H. Hall. (Transactions of the American Foundrymen's Society, 1949, vol. 57, pp. 1–23). The author surveys the literature on the use of steel castings in welded assemblies. Thermit welding and the properties of weld metal and parent metal are discussed. There are 75 illustrations of castings and welded assemblies.
R. A. R.

Oxygen Injection Applied in Steel Foundry Melting. G. E. Bellew. (American Foundryman, 1949, vol. 16, Nov., pp. 24–27). In acid electric furnace practice oxygen injection through a 'lance' is usually commenced when all the charge has melted; the power is turned off and the electrodes are raised before injection. With a top-charge furnace, the roof may be raised slightly to provide a draught and improve visibility through the working door. Residual manganese is higher in the bath when injecting oxygen than when using ore. The steel is found to contain less hydrogen with oxygen practice than with ore practice.—R. A. R.

Some Factors in Side-Blown Converter Design and Practice. A. G. Robiette. (Iron and Coal Trades Review, 1950, vol. 160, Jan. 27, pp. 181–184). In this review of side-blown converter practice the author discusses the relationship.

between design and high rate of output consistent with good high-temperature metal, long lining life, and low metal loss. Notes are included on refractories, blowers, speed control, tilting gear, and future developments.—J. C. R.

The Scope and Limitations of the Cupola/Side-Blown Converter Process. F. Cousans. (British Iron and Steel Research Association : Conference on Foundry Steel Melting, Sept. 22–23, 1949, pp. 6–7). The cupola/side-blown-converter process is shown to be a very flexible process for producing high grades of steel for castings. Great skill and careful control are required today because of the inferior quality of coke. The high final bath temperature obtained makes it possible to store several heats in suitable ladles until sufficient steel has been accumulated, and still have a sufficiently high temperature for pouring large castings of heavy section.

R. A. R.

Side-Blown Converter Design. A. G. Robiette. (British Iron and Steel Research Association : Conference on Foundry Steel Melting, Sept. 22–23, 1949, pp. 8–9). In the author's view a 2-ton converter should have a blower capable of delivering 3300 cu. ft./min. of free air at a pressure of 4–5 lb./sq. in. For adequate reaction about 5 sq. ft. of surface area per ton capacity of converter are needed ; this gives a well depth of about 12 in. Deep baths can be operated at a slow blowing rate, taking about 25 to 30 min. to avoid a high ejection loss. A converter with a more or less hemispherical bottom would have many advantages over the present cylindrical section, as in the latter the metal in the corners of the well remains relatively inactive until a boil occurs, when this high-carbon metal reacts violently with the hot, highly oxidized, low-carbon surface metal, causing excessive effervescence and ejection loss.—R. A. R.

The Aerodynamical Aspects of Side Blown Converters. M. P. Newby. (British Iron and Steel Research Association : Conference on Foundry Steel Melting, Sept. 22–23, 1949, p. 10). Experiments to study the flow of air in side-blown converters are referred to. It is suggested that converters be built with two sets of tuyeres more or less opposite each other, to produce a helical motion of blast, moving upwards through the chamber with the back eddy confined to a narrow stream down the centre of the chamber.—R. A. R.

The Control of Sulphur and Phosphorus in the Cupola/Converter Process. A. J. Langner. (British Iron and Steel Research Association : Conference on Foundry Steel Melting, Sept. 22–23, 1949, pp. 15–16). Bubbling nitrogen at the slag–metal interface helps to remove sulphur, whilst a double ladle treatment achieves an even better mixing of slag and metal. With the exception of calcium nitride (which is at present only of laboratory interest) no markedly better desulphurizing agent than sodium carbonate has been tested. A mixture of sodium carbonate and mill-scale will reduce the phosphorus in low-silicon iron by 35%, but if the silicon is high only 5–15% of the phosphorus is removed. Additions of small quantities of basic oxidizing material such as barium oxide can remove up to 45% of the phosphorus.—R. A. R.

The Application of Oxygen Enrichment to the Cupola/Converter Process. W. C. Newell. (British Iron and Steel Research Association : Conference on Foundry Steel Melting, Sept. 22–23, 1949, pp. 17–19). It is shown that in practice oxygen enrichment shortens the time necessary for initial supply of molten metal from a cupola, as well as its melting rate, in a very satisfactory manner. The greatest value from oxygen enrichment probably arises from the increased flexibility of control and from the increased output from existing plant.—R. A. R.

The Specialised Control of the Electric Arc Process for Foundry Use. J. H. Pearce and W. Bramhall. (British Iron and Steel Research Association : Conference on Foundry Steel Melting, Sept. 22–23, 1949, pp. 24–26). Melting practices for the acid and the basic arc furnaces to make steel for castings are described.—R.A. R.

Electrical Characteristics, Output and Design of Arc Furnaces. J. C. Howard. (British Iron and Steel Research Association : Conference on Foundry Steel Melting, Sept. 22–23, 1949, pp. 32–37). The design of modern arc furnaces for melting steel is discussed. Many improvements in the transformer and switching gear have been carried out. The various makers' furnaces differ more in detail than in fundamentals. With furnaces of about 10 tons capacity, about 600 kVA. transformer capacity per ton of charge is required for a melting time of 1 hr. and approximately proportionately more for lower ratings. Electromagnetic stirring by a coil underneath the furnace does not speed up melting or oxidation during the vigorous boiling stage, but it does help to remove the carbon in the lower range—say, below 0·1%, as well as the sulphur at very low sulphur contents.—R. A. R.

The Use of the Open Hearth Process in Foundries. J. Mowat. (British Iron and Steel Research Association, Conference on Foundry Steel Melting, Sept. 22–23, 1949, pp. 38–41). The economic aspects of operating acid and basic open-hearth furnaces and basic electric furnaces to make steel for castings are considered. It is shown that if the furnace can be at or near its full capacity, it is more economical to use the open-hearth furnace than its next rival the electric arc furnace.

R. A. R.

Steel Foundry Productivity. F. A. Martin. (British Iron and Steel Research Association : Conference on Steel Foundry Melting, Sept. 22–23, 1949, pp. 42–46). The author, who led the Productivity Team which visited foundries in the U.S.A., gives reasons why output is higher in American steel foundries than in Great Britain. One of the main reasons is the higher transformer capacity. The average in the U.S. foundries visited by the team is in excess of 500 kVA. per short ton, which is much higher than in Great Britain.—R. A. R.

Foreign Steel Foundry Melting Practice. A. C. Brearley. (British Iron and Steel Research Association : Conference on Foundry Steel Melting, Sept. 22–23, 1949, pp. 47–52). After some remarks on the manner in which German foundry melting practice differs from that in Great Britain, the author describes American acid electric melting technique. Where oxygen injection is practised, the blowing time to reduce the carbon from 0·35 to 0·18% is about 3 min. Tap to tap cycles range from 1¼ to 2¼ hr. with charge weights of 7000 to 14,000 lb. and production rates of 2 to 4 long tons/hr. Electricity consumption varies between 550 and 650 kWh./long ton, and electrode consumption from 7 to 10 lb./long ton.—R. A. R.

The Use of the High Frequency Process in Foundries. C. McNair. (British Iron and Steel Research Association : Conference on Foundry Steel Melting, Sept. 22–23, 1949, pp. 53–55). The advantages of high-frequency melting for foundries are : (1) Flexibility ; (2) ease of metal temperature control ; (3) conservation of alloys ; (4) freedom from defects ; (5) yield ; and (6) operating costs. The practice is described.

R. A. R.

The Design of the High Frequency Furnace. J. C. Howard. (British Iron and Steel Research Association : Conference on Foundry Steel Melting, Sept. 22–23, 1949, pp. 56–58). The capacity, frequency, and capital cost in relation to other melting furnaces, of the high-frequency induction furnace are discussed.—R. A. R.

The Fluidity of Different Steels. J. E. Worthington. (British Iron and Steel Research Association : Conference on Foundry Steel Melting, Sept. 22–23, 1949, pp. 59–66). The fluidity of steels is discussed and curves are presented to show the effects of increasing amounts of carbon, chromium, nickel, molybdenum, aluminium, and titanium on the fluidity at different temperatures. Chromium increases the fluidity of steel at all temperatures below about 1560° C. Steels containing 1% and 3% have approximately the same fluidities in the 1450–1600° C. range. Molybdenum, as well as aluminium and titanium, decrease the fluidity.—R. A. R.

The Cost of Melting in Foundries. F. N. Lloyd. (British Iron and Steel Research Association : Conference on Foundry Steel Melting, Sept. 22–23, 1949, pp. 67–71). The author outlines the principal elements of costs entering into the production of liquid steel for use in the steel foundry, and their effect on the total cost of the processes.—R. A. R.

High-Frequency Electric Furnaces for Melting and Casting Ingots under Vacuum. (Journal du Four Electrique, 1948, vol. 57, Nov.–Dec., pp. 123–126). High-frequency electric furnaces, for the vacuum-melting and casting of ingots are illustrated with diagrams and photographs. The capacity of these furnaces normally varies between 2 and 20 kg. for laboratories and 40 and 150 kg. for industrial uses. The frequency can reach 450,000 cycles/sec. for special furnaces used for research. These furnaces are made by the Ateliers de Constructions Electriques de Charleroi.—R. F. F.

Moisture in Bentonite Influences Strength. B. H. Booth. (American Foundryman, 1949, vol. 16, Aug., pp. 50–51). As

bentonite is usually evaluated by the green compression strength that it imparts to the sand with which it is mixed, the effect of the moisture content of the bentonite in the as-received condition on the potential strength of the bentonite has been studied. The tests are described and the following conclusions are reached: (1) Bentonites as supplied do differ in moisture content. (2) Low moisture content is desirable as more strength is developed per pound and freight charges are reduced. (3) Variations in moisture content of different loads of bentonite are apt to cause fluctuations in properties of foundry sand mixtures. (4) Bentonites show basic differences in potential strength even after the moisture variable has been eliminated.—J. C. R.

Molding Sand Standardized. J. J. Silk. (American Foundryman, 1949, vol. 16, Sept., pp. 51–53). Recommendations on moulding sand for a jobbing foundry producing grey iron castings are made. The percentages of sea coal recommended for different casting thicknesses are 6% for $\frac{1}{16}$ to $\frac{1}{4}$ in., 8% for $\frac{1}{4}$ to $\frac{5}{8}$ in., 10% for $\frac{5}{8}$ to $1\frac{1}{2}$ in., $12\frac{1}{2}$% for $1\frac{1}{2}$ to $2\frac{1}{2}$ in., and 15% for over $2\frac{1}{2}$ in. The maximum safe limit for water is 4%.—R. A. R.

Ninth Annual Report on Investigation of Properties of Steel Sands at Elevated Temperatures. J. P. Fraser and P. E. Kyle. (Transactions of the American Foundrymen's Society, 1949, vol. 57, pp. 89–99). Data are presented and discussed on the hot compressive strength characteristics of two sand mixtures for steel castings. Curves for compressive strength in relation to temperature, and expansion in relation to time at temperature are shown.—R. A. R.

Sand Properties *vs.* *p*H. B. H. Booth. (Transactions of the American Foundrymen's Society, 1949, vol. 57, pp. 210–221). The effect of increasing additions of Na_2CO_3 on the *p*H values of foundry sands has been studied. To increase the green strength of certain sand mixtures by *p*H control it is necessary to add only a very small amount of Na_2CO_3. The dry strength showed the largest percentage increase of all the properties tested. The dry strength increased almost directly with the *p*H value. Permeability is definitely improved by increasing the *p*H value.—R. A. R.

The New Mineral Bentonite—Its Composition and Applications in Various Industrial Fields. R. M. de Rotaeche e Iznardi. (Boletin Minero e Industrial, 1949, vol. 28, Dec., p. 569). [In Spanish]. This is a brief abstract of a paper presented by the Director of the Industrial Centre of Vizcaya. The author describes the structure of bentonites and the result of X-ray tests and goes on to mention the uses of bentonites in the manufacture of moulds. He discusses some misconceptions and the causes of confusion in the use of these materials and suggests that there was room for further study by the Spanish Iron and Steel Institute.—R. S.

HEAT-TREATMENT AND HEAT-TREATMENT FURNACES

Casting Alloys for Permanent Magnets. T. A. Dickinson. (Steel, 1949, vol. 126, Jan. 9, pp. 48–50, 74). The casting and heat-treatment of permanent magnets of Alnico is described; heat-treatment may include cooling in a strong magnetic field. Final finishing to size involves grinding, which is readily possible with standard equipment if cooling is adequate and pressures are low.—J. P. S.

Controlled Atmospheres—Principles and Applications in the Ferrous Field. D. M. Dovey and I. Jenkins. (Iron and Steel, 1949, vol. 22, Dec., pp. 645–648; 1950, vol. 23, Jan., pp. 33–36; Feb., pp. 69–72; Mar., pp. 105–107). In the first part the authors consider three groups of reactions during the heat-treatment of a metal, *viz.* (1) metal and gas react to form a compound and a second gas; (2) an alloy and a gas react to bring one constituent of the alloy out of solution and to form a second gas, *e.g.*, $C_{Fe} + CO_2 = Fe + 2CO$; and (3) the constituents of a furnace atmosphere react, either in the body of the gas or on a metal surface which may act as a catalyst. The laws governing diffusion are explained. The following gas–steel reactants are discussed in this part and in Part II: Nitrogen, oxygen, hydrogen, carbon, metal coatings, sulphur, ammonia, a N_2–H_2–H_2O mixture, a N_2–CO–CO_2 mixture, and sulphur-containing atmospheres. Some typical generated atmospheres and applications of controlled atmospheres are then described. Finally, in Part IV, these applications are classified into five groups and future developments are discussed.—R. A. R.

The Carbonitriding Process of Case Hardening Steel G. W. P. Rengstorff, M. B. Bever, and C. F. Floe. (Meta Progress, 1949, vol. 56, Nov., pp. 651–656). The carbonitriding process is described and the properties of the case are discussed. Carbonitriding can be carried out at temperatures several hundred degrees Fahrenheit below the usual carburizing temperatures. The nitrogen content of the case is high after treatment at 1300° F., but it decreases as the operating temperature is raised. The outer layer consists of carbon–nitrogen–iron compounds. The compound layer formed at 1300° F. and the inner layer formed at all temperatures change in composition and structure with depth. More and more austenite is replaced by martensite with increasing depth. The outer layer decreases in thickness with increasing temperature of treatment and may disappear at 1500–1550° F., while at the same time the martensite in the inner layer increases and this raises the hardness. Carbonitriding periods of less than 1 hr. have been used successfully. In a two-stage process (first at 1500° F. or higher, then a shorter period at 1375° F. or lower) a thicker compound layer tends to be built up without appreciable increase in the nitrogen content of the inner layer.

Some of the atmospheres used and applications of the process are described.—R. A. R.

Electronic Selective Hardening. A. H. Allen. (Steel, 1949, vol. 126, Jan. 9, pp. 46–47, 64). The Burroughs Adding Machine Co., Detroit, uses high-frequency heating for the heat-treatment of hundreds of millions of small parts per year. A wide range of heating coils has been designed which can be plugged very simply into the four 1·5 kW., 510,000–540,000 cycle induction-heating units which have been installed. The same gear is also used for silver brazing.

J. P. S.

Operational Experience with the Direct Resistance Heating for the Patenting of Steel Wire. K. Zankel. (Stahl und Eisen, 1950, vol. 70, Jan. 19, pp. 58–62). An account is given of the development of the electric resistance heating of steel wire for patenting, beginning with the first experimental plant in Austria and its modification, and then describing a second new plant. Operating data for this plant and for electrically heated muffles for the same purpose are compared, and the excellent properties of the wire produced are mentioned.

The Applicability of Isothermal Hardening in the Production of Unalloyed Steel Wire. A. Pomp and G. Gesche. (Stahl und Eisen, 1950, vol. 70, Jan. 19, pp. 52–57). Wires 3·44–3·46 mm. in dia. of three kinds of steel (C 0·37%, 0·50%, and 0·62%, respectively) were quenched from 925° C. into salt baths at 300° to 450° C. and patented. They were then reduced 90·7% by drawing; the drawing force and the mechanical properties of the product were determined. The results indicated that the salt-bath-quenched and drawn wire did not have as good bending and twisting properties as patented and drawn wire.—R. A. R.

Metallurgical Control of Coil Annealing in Radiant Convector Furnaces. G. B. Espey. (Iron and Steel Engineer, 1949, vol. 26, Dec., pp. 99–107). A brief description is given of the principles of vertical cylindrical annealing furnaces with high-speed convection heating, with details of tests of the rate of heating and temperature distribution when annealing coils of steel strip in this and in older types of furnace. The chief differences between the high-convection radiant convector type and the low-convection type furnaces are: (1) The small impeller fans have been replaced by centrifugal turbine-type fans which circulate the protective atmosphere at a much higher velocity; (2) the circular base plate is now supported by a ring of 'diffuser' blades which deliver the gases from the fan into a narrow annular space between the cylindrical inner cover and its sleeve liner; (3) the sleeve liner has been added to the inner cover to keep the gases at high velocity and greatly increase the heat transfer and the heating surface area; (4) after being heated, the gases travel into 'convector plates' between the coils; these four changes make each stack of coils and its inner cover into an integrated heat exchanger; (5) the combustion capacity of each tube assembly in the portable furnaces placed over the exchanger stacks has been increased to provide for the much higher rate of heat absorption. The new type of furnace enabled coils of larger diameter to be annealed efficiently and shortened the batch annealing cycle by 50–65%.—R. A. R.

Operating Costs Cut and Efficiency Improved by Normalizing Procedure Used in the Manufacture of High Pressure Gas Cylinders. L. E. Browne. (Steel, 1949, vol. 125, Dec. 26, pp. 53–54). A furnace for normalizing high-pressure gas cylinders is described; its special feature is a preheating zone kept at 1950° F. (1066° C.) which is 500° F. (278° C.) higher than the working temperature of 1450° F. (788° C.). This gives more rapid heating to the working temperature.—J. P. S.

Researches on the Manufacture of Metal-Cutting Saws. Report I. Researches on a New Method of Hardening Hack Saw Blades. M. Okoshi and K. Watanabe. (Bulletin of The Institute of Physical and Chemical Research, vol. 22, No. 2, pp. 119–144). [In Japanese].

Researches on the Manufacture of Metal-Cutting Saws. Report II. Researches on a Method of Hardening Saw Blades. M. Okoshi and K. Watanabe. (Bulletin of The Institute of Physical and Chemical Research, vol. 22, No. 11, pp. 941–957). [In Japanese].

Oxy-Acetylene Flame Hardening in Commercial Heat Treatment. J. T. Howat. (Welding Journal, 1949, vol. 28, Nov., pp. 1043–1052). Flame-hardening is a very effective means of providing a hard-wearing surface on a material having a ductile core; it requires the least equipment and space of any hardening process. The present article describes and illustrates a number of applications such as the flame-hardening of machine-tool bed ways, steam-shovel roller pads, clutch gear teeth, spur gears, mill rolls, and coupling boxes, etc. J. P. S.

What to Do about Temper Brittleness of Steels. L. D. Jaffe. (Steel, 1949, vol. 125, Nov. 21, pp. 86–89, 114). Investigations on temper brittleness are reviewed and examples of it and the influence of heat-treatment are illustrated by graphs. The following are some of the recommendations made to reduce its effect: (1) Steel tempered at above 1000° F. should be cooled rapidly; (2) a short tempering time at a high temperature is better than a longer time at a lower temperature; (3) use a steel which is tough before heat-treatment; (4) keep the contents of manganese, chromium, nickel, and vanadium as low as hardenability requirements will permit; (4) keep the phosphorus as low as possible; and (5) use molybdenum in the steel.—R. A. R.

Modern Evaluation of Heat-Treatable Alloy Steels. E. Folkhard. (Berg- und Hüttenmännische Monatshefte der Montanistischen Hochschule in Leoben, 1950, vol. 95, Jan., pp. 1–8). The Jominy end-quench hardenability test is described and results obtained with it on several low-alloy steels are presented and discussed. It is shown how the test can be used to predict the tempering temperatures required to produce a given strength.—R. A. R.

FORGING, STAMPING, DRAWING, AND PRESSING

A £1,000,000 Forging Plant. (Machinery, 1950, vol. 76, Apr. 27, pp. 591–597). The new forging plant at the Bromsgrove Works of John Garrington and Sons, Ltd., is described. Twelve forging presses each with its stripping press and high-frequency heaters for heating the billets are used. One is a 5000 tons press, two are 2000, three 1000, four 800, and two 500 tons. Croppers are used for cutting the bars into billets, electric furnaces for hardening and tempering or normalizing the forged products, and a shot-blasting plant is provided. The finished forgings range in weight from a few ounces to upwards of 60 lb. and the yearly production will be 20,000 tons of steel forgings.—R. F. F.

Cupping Thick Steel Blanks. G. Sachs, G. Espey, and J. Taub. (Steel, 1949, vol. 125, Nov. 7, pp. 112–115; Nov. 14, pp. 87–94). Experiments on the forming of cups from thick steel discs have shown the following results: The diameter must be reduced more than 20% or the disc will slip through the die, and if the punch diameter is less than 50% of the disc diameter, the bottom will be punched out. If the reduction of wall thickness is more than 30%, and if the reduction in diameter is more than 30%, tensile failure will occur in the wall of the cup. Even-edged cups can be produced only within a certain range of diameter and wall reduction, about 25% in each case, but varying with die design: a design having a small entrance radius and a straight taper favours this.—J. P. S.

Better Press Performance Expected in Asymmetrical Deep Drawing Operations. W. T. Lankford, S. C. Snyder, and J. A. Bauscher. (American Society for Metals: Steel, 1949, vol. 125, Dec. 19, pp. 82–86). A study has been made of low-carbon deep-drawing steel sheets from 46 lots of fully killed steel. Of these, 29 had produced much die scrap in pressing operations and 17 lots were representative of good performance. True stress–strain curves were determined on a new type of recording torque magnetometer, and ordinary mechanical properties were determined by conventional techniques. It has been generally believed that material substantially free from directionality in plastic properties would give the best performance in pressing, but the present tests, which included drawing motor-car fenders involving severe biaxial stretching of an asymmetrical nature, demonstrated that material having considerable plastic anisotropy of a favourable nature gave the best performance, whereas fenders formed from a nearly isotropic material exhibited a very severe localization of strain.—R. A. R.

Production of Wire and Wire Rods. K. B. Lewes. (Steel, 1949, vol. 125, Dec. 26, pp. 58, 60–61, 63–64, 66–67; vol. 126, Jan. 9, pp. 66, 68, 71–72, 74; Jan. 16, pp. 70, 73–74, 76, 79). The author first deals with the history of wire drawing and wire rod rolling, paying tribute to the contributions of Bedson, Morgan, and Garrett in developing rod mills. The modern mill is of the Morgan type, continuous, with up to four strands, and separately controlled finishing stands. He then describes the pickling process and the liming and baking of rods for drawing, and deals with the functions of lubricants. Various types of continuous wire-drawing machinery are next dealt with and followed by descriptions of annealing processes. Galvanizing is next studied, both by hot-dipping and electro-galvanizing methods, and the manufacture of wire nails, barbed wire, and woven wire is included. The series concludes with a short note on back-pull wire-drawing.—J. P. S.

Experience and Development in the American Wire Industry since 1939. H. Höhle. (Stahl und Eisen, 1950, vol. 70, Jan. 19, pp. 41–51). The American wire industry, including rolling, drawing, heat-treatment, galvanizing, barbed-wire manufacture, and screen and wire-rope making, is reviewed and many illustrations are presented. Coil sizes have been increased up to a maximum of 425 kg. and wet drawing speeds up to 15 m./sec. have been attained. These and other improvements have increased output considerably since 1939.—R. A. R.

ROLLING-MILL PRACTICE

Blooming Mill Operations at Keystone Steel and Wire Co. W. Herman. (Iron and Steel Engineer, 1949, vol. 26, Dec., pp. 88–91). A blooming mill at the works of Keystone Steel and Wire Co., Peoria, Illinois, is described. This mill was erected in 1917 and is now driven by a 2500-h.p. D.C. motor, with electrically driven side guards and screwdowns. The two-high stand has rolls 96 in. long and 28 in. in dia. Ingots 16 × 18 in. can be rolled down to 1¾ in. billets in 25 passes, 21 passes being required to break down the ingot to 3¼ in. square. Modifications have been made from time to time to enable the mill to keep pace with increased furnace capacity. R. A. R.

Problems in Speeding-Up Strip Mills. F. Mohler. (Iron and Steel Engineer, 1949, vol. 26, Dec., pp. 92–98). The author makes proposals for dealing with the difficulties involved in the design of motors for high-speed wide strip mills.

Cold Rolling Technique. Part III—The Effect of Strip Tension on Mill Power. Part IV—Simplified Rolling Mill Calculations. Part V—Resistance of Materials to Deformation. H. Ford. (Sheet Metal Industries, 1949, vol. 26, Jan., pp. 81–86; Feb., pp. 315–318; Apr., pp. 733–741; May, pp. 960–962; June, pp. 1205–1208; July, pp. 1427–1435; Aug., pp. 1651–1656, 1666; Sept., pp. 1889–1893; Oct., pp. 2109–2114; Nov., pp. 2333–2340). Continuation of a series of articles (*see* Journ. I. and S.I., 1949, vol. 161, Apr., p. 380).

MACHINERY FOR IRON AND STEEL PLANT

Investigation of the Power Required for Cutting by Shearing along a Straight Line. F. Keller. (Iron and Steel Institute, 1950, Translation Series, No. 401). This is an English translation of a paper which appeared in Werkstatt und Betrieb, 1949, vol. 82, May, pp. 165–171 (*see* Journ. I. and S.I., 1950, vol. 164, Feb., p. 237).

Stresses in Hot Metal Ladles. K. E. Knudsen, W. H. Munse, and B. G. Johnston. (Iron and Steel Engineer, 1949, vol. 26. Dec., pp. 49–70). Extensive experimental and theoretical stress analyses of models representing hot-metal ladles of three types have been made. The types were the round riveted, the oval welded, and the round welded with dished bottom. One-fifth scale models loaded with mercury were used and stresses were calculated from determinations with electrical resistance strain gauges. The principal conclusions were : (1) Under load, side deflections vary approximately linearly from zero at the bottom to maximum at the lip ; this deflection is inwards in the trunnion region and outwards between the trunnions. (2) Stresses in the stiffener rings are highest at the trunnion line and midway between the trunnions. The lip ring carries the largest stresses, and the lower stiffener the smallest. (3) The side shell suffers only small stresses, except near the bottom juncture where large discontinuity stresses are found. (4) Flat bottoms have very large deflections, and the stresses at both centre and edge are likely to exceed the yield point. (5) Dished bottoms show moderate deflections and stresses and are superior to the flat types. (6) Stresses and deflections increase nearly linearly with both load and distance between the ladle crane hooks, except for bottom stresses which are unaffected by the latter. (7) Tilting the ladle does not increase the stresses. (8) No major difference in structural behaviour was found between riveted and welded ladles. (9) Wider trunnion assemblies tend to reduce the stiffener-ring stresses. (10) A spacer band or a heavy middle shell portion reduces the stiffener-ring stresses approximately in proportion to the dead weight added by these members.—R. A. R.

A Network System for Dynamic Lowering Hoist Control. D. L. Pettit. (Iron and Steel Engineer, 1949, vol. 26, Dec., pp. 71–79). The circuit described uses a minimum number of contactors to obtain six speeds of a series-wound D.C. motor for crane hoisting and lowering motions.—R. A. R.

Open Hearth Electrical Equipment. S. Rifkin. (Blast Furnace and Steel Plant, 1949, vol. 37, Dec., pp. 1451–1455). The electrical gear required for the control of stockyard magnet cranes, charging machines, and hot metal and ladle cranes, is described.—J. P. S.

Cab of Slag Shovel Air Conditioned. R. A. Merck. (Blast Furnace and Steel Plant, 1949, vol. 37, Dec., pp. 1466–1468). At the Pittsburgh works of the Jones and Laughlin Steel Corporation, there is no room for the permanent disposal of blast-furnace slag ; it is therefore dumped in a temporary pit and removed by a local company for processing into building blocks, road materials, etc. The heat encountered in removing the slag with an electric caterpillar shovel, and the fumes generated when the slag is sprayed with water have necessitated the installation of a crane-cab cooler to improve the operator's working conditions and to protect the electrical and mechanical equipment.—J. P. S.

Blast-Furnace Gas Boosts Steam Plant Output. P. J. Berg. (Blast Furnace and Steel Plant, 1949, vol. 37, Dec., pp. 1476–1478). A steel company in Pennsylvania has recently installed new boiler plant which utilizes 2,500,000 cu. ft./day of blast-furnace gas of 110 B.Th.U./cu. ft. which had previously been wasted to atmosphere. Two boilers each producing 200,000 lb./hr. of steam at 850 lb./sq. in. and total temperature of 850° F., have been installed ; most of this steam is supplied to a 7500-kW. 25-cycle turbine, the exhaust from this and the remainder of the boiler supply, after de-superheating and pressure reduction, is passed to the steel mill at 165 lb./sq. in.—J. P. S.

Various Methods for Calculating the Efficiency and Regulation of Transformers and their Effect on the Economy of the Apparatus. A. Pelayo Toribio. (Anales de Mecanica y Electricidad, 1949, vol. 25, Nov.–Dec., pp. 336–346). [In Spanish]. The analytical and graphical methods of calculating the efficiency and regulation of transformers are explained.—R. S.

WELDING AND FLAME-CUTTING

Power Supply for Metal Arc Welding. C. A. Kershaw. (Welding, 1949, vol. 17, Nov., pp. 486–492). The welding characteristics of both alternating and direct current supply systems are considered with reference to developments which have taken place to overcome the disadvantages of the former. The effects of introducing condensers for power factor correction are discussed together with the question of unbalance on the three-phase mains when using single-phase welding transformers.—R. A. R.

Analyzing Metal Transfer in Arc Welding. R. C. McMaster, D. C. Martin, and A. Leatherman. (Welding Journal, 1949, vol. 28, Dec., pp. 575-s–583-s). The transfer of metal across the welding arc may take place either by the formation of globules of molten metal which momentarily short-circuit the arc or by the development of a spray of molten particles which does not. Conditions in the former case have been studied with a specially designed short-circuit analyser ; this is connected across the arc and operates when the arc voltage drops in short-circuit conditions. It can be made to indicate the number of short-circuits per second, the average duration, and the number of more than a given duration. It has been found that the number of short-circuits is greatest with bare-wire electrodes, and is greatly affected by the character of the electrode coating, and diminishes in all cases as the arc voltage rises ; this last factor is a natural corollary of the increase in arc length.—J. P. S.

The Statistical Part in Welding Investigation. B. B. Day. (Welding Journal, 1949, vol. 28, Oct., pp. 449-s–459-s). The theory of the application of statistical analysis to the study of welded joints is considered, with especial reference to the use of factorial combination.—J. P. S.

Development of Specimen Simulating Weld Heat-Affected Zones. E. F. Nippes and W. F. Savage. (Welding Journal, 1949, vol. 28, Nov., pp. 534-s–545-s). An electronic device is described which makes possible very quick and accurate control of the temperature and rate of cooling of a specimen held between the jaws of a flash welder. The object of this procedure is to simulate the thermal effects of the deposition of weld metal. A thermocouple is attached to the midpoint of the specimen, and the voltage generated is balanced against the voltage produced by a potentiometer operated by a cam shaped according to the programme to be followed ; the out-of-balance voltage is amplified and used to correct the divergence from the programme.—J. P. S.

Tests of Specimens Simulating Heat Affected Zones. E. F. Nippes and W. F. Savage. (Welding Journal, 1949, vol. 28, Dec., pp. 599-s–616-s). Using the electronic device designed by the authors for simulating the conditions in and near the heat-affected zones of a welded joint (*see* preceding abstract) the impact properties of the heat-affected zones have been studied. It has been found possible to duplicate any of the microstructures found near an arc weld : a systematic study was carried out of the properties of a weld made in $\frac{1}{2}$-in. plate with an energy input of 70,000 joules/in. This revealed that the coarsened region next to the weld gave poorer impact properties the higher the maximum temperature reached ; a region further from the weld than the zone usually considered to be heat-affected had the poorest impact properties of any investigated, and this is attributed to a strain-ageing phenomenon. In this region the maximum impact strength is only one half of that of the original plate, and the transition temperature is higher, by 20–50° F. depending on the criteria used. Further investigations by the technique are promised, including the high-temperature graphitization of molybdenum steels, the sensitizing effect of the welding of stainless steels, and tempering effects on alloy steels.—J. P. S.

Cooling Rates in Arc Welds in $\frac{1}{2}$-in. Plate. E. F. Nippes. L. L. Merrill, and W. F. Savage. (Welding Journal, 1949, vol, 28, Nov., pp. 556-s–565-s). A series of differential equations has been developed, based on quantitative temperature measurements in the neighbourhood of arc welds in $\frac{1}{2}$-in. steel plate, which express the temperature distribution in terms of time, distance from weld centre-line, and welding variables. Graphical solutions, which are also included, permit calculation of the heating and cooling cycles at any point in the vicinity of an arc weld, in plate of this thickness.—J. P. S.

Developments in Automatic Hard Facing. H. W. Sharp. (Welding Journal, 1949, vol. 28, Nov., pp. 1037–1039). Automatic arc-welding machines are being used for the hard facing of crusher cones, rollers, mill-brake-drums, etc. Electrodes are often supplied in tubular form, with the alloying elements in granular condition inside them.—J. P. S.

Cracking in Heavy Forged Flanges of Oil Separators. H. B. Fergusson and P. L. J. Leder. (Welding Journal, 1949, vol. 28, Nov., pp. 521-s–526-s). In the welding of heavy forged rings on to cylinders 4 ft. 6 in. in dia. and 3 in. wall thickness,

difficulty was experienced with cracks which appeared in the flanges, running circumferentially a little distance above the weld spigot. The cause was believed to be the severe restraint produced by the heavy flange section, allied to the facts that the steel tended to rupture along cleavage planes under complex stresses, that it had a slightly high brittle-ductile transformation temperature and in addition formed intergranular carbide films under certain conditions of heating and cooling. The cracking is entirely eliminated by preheating the flange to 100° C.—J. P. S.

Heliarc and Railroad Applications. H. E. Gannett. (Welding Journal, 1949, vol. 28, Dec., pp. 1147–1151). The inert-gas-shielded arc-welding process has been used on the Burlington Railroad for the repair of cast-iron cylinder heads and for the fixing of stainless steel sheeting to the members of passenger coaches.—J. P. S.

Influence of Consumption Rates on Flash Welding. W. N. Platte. (Welding Journal, 1949, vol. 28, Dec., pp. 584-s–598-s). Flash-butt welding has been studied from the point of view of material consumption rate (*i.e.*, the amount of metal expelled in the welding process), the voltage and current supplied, and the temperature of the work during the process. Among the conclusions are: (1) The minimum permissible voltage is a function of the flashing rate (*i.e.*, the rate of approach of the pieces being joined), the dimensions of the pieces, and their temperature; (2) the current required increases as the flashing rate increases; and (3) the rate of temperature increase depends on the flashing rate.—J. P. S.

How to Weld Sheet Steel. K. H. Koopman and F. J. Pilia. (Welding Journal, 1949, vol. 28, June, pp. 563–566; Oct., pp. 976–977). The first part of this article gives practical advice, with clear illustrations, for simple operations involving the gas-welding of sheet steel up to $\frac{1}{8}$ in. in thickness. The second part deals with the use of the inert-gas-shielded arc processes.—J. P. S.

Spot Welding of Heavy Gauge Structural Steel. E. F. Nippes and R. F. Underhill. (Welding Journal, 1949, vol. 28, Oct., pp. 507-s–520-s). As a result of experiments described it has been found that $\frac{1}{4}$-in. steel sheet in the pickled condition, and $\frac{3}{16}$-in., $\frac{1}{4}$-in., $\frac{3}{8}$-in., and $\frac{1}{2}$-in. plate in the grit-blasted condition can be satisfactorily spot-welded. In the three lower gauges, to obtain a ratio of tensile strength to shear strength exceeding 45, it is necessary to temper the welds. This is best done by cooling the weld and then reheating to tempering temperature with additional current while the material is still between the electrodes.—J. P. S.

Fabrication of Large Alloy-Steel Shovel Buckets. E. R. McClung. (Welding Journal, 1949, vol. 28, Dec., pp. 1133–1141). The use of welding in the construction of very large buckets of 50 cu. yd. capacity for dipper shovels is described. A comparatively simple design was worked out, and constructed of a steel of the following composition: 0·15–0·20% of carbon, 1·5% of manganese, and 0·40–0·50% of molybdenum. The parts of the assembly requiring greatest wear-resistance were made from an austenitic steel containing 0·35% of carbon, 13% of manganese, 3·25% of nickel, 4·25% of chromium, and 0·45–0·50% of molybdenum; a great advantage of this is that it is readily weldable with austenitic electrodes; these can also be used for welding this steel to the manganese–molybdenum steel. For the welding of the latter to itself, lime ferritic electrodes, E 10016, were used.—J. P. S.

An Evaluation of the Resistance Welding of Tin and Tin–Zinc Alloy Coated Mild Steel Sheet. A. J. Hipperson and P. M. Teanby. (Transactions of the Institute of Welding, 1949, vol. 12, Oct.: Welding Research, vol. 3, pp. 86r–92r. Tests have been made on the spot-welding of auto-body quality steel sheet, of 0·01 in. thickness covered with (*a*) tin, 0·0001 in. thick, (*b*) 50/50 tin–zinc alloy 0·0001 in. thick, and (*c*) 80/20 tin–zinc alloy 0·0003 in. thick, and on both spot- and flash-welding of 0·05 in. material similarly coated. Three types of electrode material were also tested, hard-drawn high-conductivity copper, cadmium–copper, and chromium–copper. Tin–zinc alloy coatings were found to be better suited than plain tin to the process, as adhesion to the electrode tips becomes serious after a time with the latter, the chromium–copper electrodes resisting the effect better than the others. With thicker coatings, higher welding currents are necessary, and electrode life is necessarily shorter. However, if proper maintenance of electrode tips is carried out, the spot-welding of coated steels presents no real difficulties.—J. P. S.

Welding of Stainless Clad Steel. P. C. Arnold. (Welding Journal, 1949, vol. 28, Oct., pp. 940–945). Types of procedure for welding stainless-clad steel are described. The use of double-**V** preparations may avoid the warpage encountered with single-**V** joints, while the use of 25% chromium 12% nickel alloy electrodes stabilized with columbium will discourage carbon penetration into the stainless weld metal.
J. P. S.

Silver Alloy Brazing Stainless Steel. C. H. Chatfield and A. W. Swift. (Welding Journal, 1949, vol. 28, Dec., pp. 1142–1146). The theory and practice of silver brazing is discussed and it is made clear that all types of stainless steel can be satisfactorily brazed, provided that the surfaces are clean and properly coated with flux, and that design of the joints is good and allows a clearance of 0·0015–0·005 in. Stress-corrosion cracking is not due, as has been alleged, to selective diffusion of zinc from the brazing alloy into the steel, but will only arise when the parts are in a state of stress before the molten alloy comes into contact with them. Corrosion resistance of these joints is high, except to nitric acid, although chloride solutions may attack the bond between the solder and the steel: the addition of nickel to the solder will obviate this. If the brazing time can be kept short, there is little danger of intercrystalline carbide deposition; this can, in the event, be minimized by the use of titanium- or niobium-stabilized varieties of stainless steel.—J. P. S.

Constitution Diagram for Stainless Steel Weld Metal. A. L. Schaeffler. (Metal Progress, 1949, vol. 56, Nov., pp. 680, 680-B). A diagram is presented for determining the approximate proportions of austenite, ferrite, or martensite which will be obtained in a given stainless steel weld metal.—R. A. R.

Welding Copper to Other Metals Speeded-up by New Process. D. Reebel. (Steel, 1949, vol. 125, Nov. 14, pp. 84–86). The Cadweld process, developed by the Electric Railway Improvement Co., Cleveland, Ohio, for joining copper conductors to each other or to steel rails, earthing rods, etc., is a thermit process which produces molten copper from copper oxide and aluminium powder. Graphite moulds are used to contain the melt. The joints are of low resistance and high current capacity.—J. P. S.

The Stress-Relieving of Welded Structures. R. Weck. (Welding, 1949, vol. 17, Oct., pp. 442–452). An English version of a paper which appeared in Revue de la Soudure/Lastijdschrift, 1949, vol. 5, No. 3, pp. 127–136. (*See* Journ. I. and S.I., 1950, vol. 166, Oct., p. 158).

Oxygen-Acetylene Scarfing in the Steel Mill. G. Mersot. (Welding Journal, 1949, vol. 28, Nov., pp. 1052–1056). The practice at Inland Steel Co., East Chicago, Ind., for scarfing billets and slabs is described. Special long-handled torches are used and the slabs and billets are frequently placed on stands at a tilt; this minimizes the fatigue of the operators, and assists the running-off of the slag. Magnets are used to handle slabs, overhead cranes, and chains for billets and blooms.
J. P. S.

Heavy Section Scrap Cutting. E. M. Holub. (Blast Furnace and Steel Plant, 1949, vol. 37, Nov., pp. 1335–1336). The Oxweld C-60 oxygen blowpipe for cutting large steel lumps up to 6 ft. thick to charging-box size is described. This has a cutting nozzle of appropriate size and a tubular powder-cutting attachment with which an iron-rich powder is blown into the oxygen stream from outside the preheating flame. Any refractory oxides are removed by a combined melting and fluxing action as the cutting proceeds. The cost of cutting with this tool is very much less than with the oxygen lance.—R. A. R.

New Methods of Oxygen Cutting Stainless Steel. E. Seymour Semper. (Transactions of the Institute of Welding, 1949, vol. 12, Oct., pp. 125–132). The author explains why gas cutting of stainless steel is extremely difficult—the alloy is hard to oxidize and the oxides have a high melting point. Cutting therefore consists largely of melting the metal and expelling it the other side of the cut; the use of a starting rod of mild steel, or of a plate of mild steel laid down over the line to be cut, may assist this. Three other methods of cutting are available, however, powder cutting, oxy-arc cutting, and flux-injection cutting; these are described. In the first an iron-rich powder is fed into the cut: this has for its chief effect the provision of additional heat through the

oxides formed and also helps to flux away the chromic oxide. The oxy-arc process, so far used only by hand, employs a hollow flux-coated electrode, oxygen being fed down the central hole: cutting proceeds by the melting of the metal and its dilution with mild steel from the electrode, whose coating has, also, a fluxing effect. In the flux injection process, a flux of, at present, unknown composition but non-metallic in appearance, is fed into the oxygen stream of the cutting blowpipe: it appears to act not only by fluxing the refractory oxides, but by mechanically removing them as they form. Working data for those three processes are given.—J. P. S.

CLEANING AND PICKLING

Electropolishing of Steel in Chrome–Acetic Acid Electrolyte. C. E. Morris. (Metal Progress, 1949, vol. 56, Nov., pp. 696–699: British Industrial Finishing, 1950, vol. 2, Feb., pp. 504–513). The author describes a chrome/acetic-acid electrolyte, of very low water content, which can be made up without recourse to acetic anhydride, a new method of making electrical contact with the specimens, and an unusual way of agitating the solution. The electrolyte (glacial acetic acid 99·5% by weight min., CrO_3 25 g., water 7 ml.) is contained in a stainless steel dish which acts as the cathode. A cooling coil of glass or stainless steel is immersed in the electrolyte, which should be ½ in. deep. The microspecimen is held in a stainless steel jig and rotated at a constant speed of 100 ± 2 r.p.m., with the working face ¼ in. away from the bottom of the dish. The operating temperature is 17–19° C. The voltage applied across the cell is 20.—R. A. R.

Studies on Electrolytic Polishing, Part I. N. Takahashi. (Bulletin of the Institute of Physical and Chemical Research, vol. 22, No. 1, pp. 1–58). [In Japanese].

Electrical Resistance of the Anodic Layer and the Optimum Composition of Electrolytic Polishing Baths. E. Darmois, I. Epelboin, D. Amine, and C. Chalin. (Revue de Métallurgie, Mémoires, 1950, vol. 47, Mar., pp. 183–186). *See* Journ. I. and S.I., 1950, vol. 166, Sept., p. 96.

Methods of Surveying Steel Plant Wastes. A. H. Arbogast and J. E. Gold. (Iron and Steel Engineer, 1949, vol. 26, Dec., pp. 80–87). Parts of United States Federal Laws relating to river pollution and industrial effluents are cited, and some of the literature on the treatment of steel-plant wastes, such as oily effluents and spent pickle liquor, is reviewed.—R. A. R.

Flame Straightening, Forming and Cleaning Structural Steel. F. H. Dill. (Welding Journal, 1949, vol. 28, Nov., pp. 1067–1069). The oxy-acetylene torch can be used for local heating, as for bending, straightening, the removal of local stresses in, for example, welded plate in ship construction, the cambering of beams by heat shrinking, and the flame-cleaning of structures before painting.—J. P. S.

PROTECTIVE COATINGS

The Protection of Surfaces against High Temperature Corrosion. (Engineering and Boiler House Review, 1950, vol. 65, Jan., pp. 13–15, 25). The processes for coating steel with aluminium, namely, aluminium spraying, dipping in molten aluminium, diffusion, and stoving an aluminium lacquer, to provide protection against high-temperature corrosion are described. To clean the steel before the dipping process, cleaning in a molten salt bath with transfer of the work piece into the aluminium bath under protective-atmosphere conditions is advocated. The Dellgren process of doing this is said to be employed in Sweden with good results. A patented process for lacquering proposes a mixture of 40 g. aluminium powder with 25 c.c. of 6% pyroxilin solution, 10 c.c. of benzol, and 5 c.c. of amylacetate.—R. A. R.

Electroplating Jigs. A. H. E. Barrow. (Metal Industry, 1950, vol. 76, Feb. 24, pp. 147–148). The use of permanent magnet jigs to carry parts in plating solutions is discussed. The magnet can be attached to the shaft of the jig by bolts, rivets or straps, but the joint must be finished with soft or silver solder to ensure sound electrical contact. The pole pieces should be bridged with a keeper when not in use. If chromium is to be the final finish, magnet jigging cannot be used until the nickel coating has been deposited, and then contact must be made on some part of the article that is non-critical for the chromium deposit. The magnet must be sufficiently strong to hold the article during vigorous washing. R. A. R.

How to Apply Metal Coatings by Vacuum Evaporation. (Steel, 1949, vol. 125, Dec. 12, pp. 84–87, 115, 116). The techniques, advantages, and limitations of applying thin metal coatings to metals or non-metallic surfaces are outlined. There are three essential parts of a vacuum-evaporation plant. First, a pumping system capable of evacuating the process vessel to an absolute pressure of 10^{-4}–10^{-5} mm. Hg; second, means of heating the metal to its evaporation temperature; and third, means of holding the work so that it will be properly exposed to the metal vapour. A rotary coating machine for the mass production of small coated objects is described. This consists of 16 bell jars, 14 in. in dia. and 18 in. high, mounted on a turntable. While one jar is being loaded, the previous one is being rough-pumped by a mechanical pump, and ten are being pumped to high vacuum. In subsequent positions the filament to evaporate the metal is degassed, the charge is melted, and finally the metal is vaporized. At the last position the jar is released to atmospheric pressure, unloaded, and prepared for recharging. The cycle can be completed in 3 min.—R. A. R.

Electrocoloring of Stainless Steels in Aqueous Solutions. C. E. Naylor. (Plating, 1950, vol. 37, Feb., pp. 153, 154, 159, 160, 171). The colouring of stainless steel in modified sulphuric acid solutions is discussed. For electrolytic colouring a solution giving good results consists of 25 vol.-% H_2SO_4 (sp. gr. 1·84) with an addition of 8 oz. sodium dichromate per U.S. gallon, with an operating temperature of 158–185° F. An anode current density of about 0·6 amp./sq. ft. at 1·0–1·3 V. was found suitable. Another method consists of simple immersion of the stainless steel for 5–10 min. in a solution preferably containing 50 vol.-% H_2SO_4 (sp. gr. 1·84) and about 1·7 oz. of sodium dichromate per U.S. gallon. The main disadvantage of this method is the difficulty in matching colours. The author, when trying the galvanic method outlined by Batcheller, was unable to confirm the latter's results, but found that stainless steel in conjunction with lead could be coloured provided that an auxiliary electrode of previously coloured stainless steel was attached to it either externally by a wire or by clamping together in solution. A current density of the order of 0·06 amp./sq. ft. was found to be adequate.—R. A. R.

Wear Resisting Characteristics of Chromium-Plating. I. I. Iitaka. (Bulletin of The Institute of Physical and Chemical Research, vol. 22, No. 6, pp. 558–570). [In Japanese].

Notes on Nickel Plating from a Fluoborate Bath. E. J. Roehl and W. A. Wesley. (Plating, 1950, vol. 37, Feb., pp. 142–146, 171). A limited survey was made of the behaviour of a nickel fluoborate electrolyte containing excess boric acid. The nickel plated from it was tough and ductile, and showed 30% less contracting stress than deposits from a Watts bath. Anode and cathode efficiencies were high, and the conductivity of the electrolyte was as high as that of the all chloride nickel bath. A disadvantage is the corrosive attack which precludes the use of lead or high-silicon cast iron, but certain corrosion-resisting steels, rubber, pyrex, and carbon satisfactorily resist attack. The fluoborate bath is a practical and easily controlled solution to employ.—R. A. R.

Continuous Coating Units. H. W. Lynn. (Blast Furnace and Steel Plant, 1949, vol. 37, Dec., pp. 1463–1465). The author describes a hot-dip coil galvanizing line recently installed by the Wean Engineering Company at Weirton Steel Company. The strip is first electrolytically cleaned and recoiled, and then annealed: it then passes through a special rolling process to flatten it without cold-working it. It now goes to the galvanizing line proper, where the leading end is squared and welded to the tail of the preceding coil, and through a side trimming shear to cut it to width. It next passes through a scrubbing unit for cleaning and through a flux bath and radiant heat drier. Now it goes through the kettle of molten zinc, and down a cooling tower to the cooling table. After this comes a final cleaning treatment, roller levelling, cutting to length, and inspection.—J. P. S.

The Manufacture of Tinplate. E. Diaz-Varela y Ceano-Vivas. (Boletin Minero e Industrial, 1949, vol. 28, Oct., pp. 439–448). [In Spanish]. Tinplate must be cheap, light, and rigid with a smooth, clean, and polished surface and must be resistant to corrosion. The author discusses the type of steel to be used and explains the process of pack rolling. He

does not believe that a modern American continuous plant can be put down in Spain for many years, not only because of the cost, but also because the rated capacities of 35,000 to 50,000 tons per month are more than the annual production in Spain, and there is not enough steel capacity.

The second part deals with the tin component and its characteristics. The immersion and electrolytic methods of coating, and the subsequent processes are described. Tables showing production, consumption, and prices abroad and in Spain, are given.—R. S.

Mass Press-Forming Figures Prominently in Steel House Production. (Steel, 1949, vol. 125, Oct. 24, pp. 64–65). The Lustron Corporation, at Columbus, Ohio, mass-produces steel panels, etc., for house construction. Structural parts, welded from sheet, are bonderized, painted, and dried, while exterior and interior panels are pickled, nickel-flashed, and porcelain enamelled.—J. P. S.

Silicone Heat-Resisting Paints. (Product Finishing, 1950, vol. 3, Jan., pp. 22–26). The development of silicone varnishes and paints is briefly described. By varying the ratio of hard and fast curing resins in the finish, varying degrees of hardness and flexibility of the film after curing can be achieved. To obtain the best adhesion, steel surfaces should be prepared by sand-blasting or phosphatizing. An aluminium-pigmented silicone paint, properly cured, has withstood a temperature of 538° C. for 40 hr. Two proprietary brands of English manufacture are described.—R. A. R.

The Surface Preparation and Repainting of Structural Iron and Steel. A. J. Eickhoff. (Proceedings of the American Society for Testing Materials, 1949, vol. 49, pp. 311–317). The results are reported of an investigation of the condition of steel panels which have been repainted after weathering of previous coats of paint with a view to: (*a*) Ascertaining the maximum degree of corrosion permissible before repainting is necessary; (*b*) comparing three chemical pretreatments; (*c*) comparing the performances of paint applied to surfaces in different conditions, and (*d*) comparing two paint systems.

The Testing of Paint. J. A. Gascoigne. (British Industrial Finishing, 1949, vol. 2, Nov., pp. 283–291; Dec., pp. 359–366). In Part I equipment and techniques for testing the viscosity, drying properties, flexibility, opacity, colour, and surface characteristics of paints are described. In Part II the tests which the meticulous paint finisher should perform are discussed; these include the determination of flash-point, water content, specific gravity, solids content, resistance to heat and grease, and pigment/vehicle ratio.—R. A. R.

The Estimation of Cobalt in Bright Nickel Plating Solutions. H. D. Carter. (Journal of the Electrodepositors' Technical Society, 1948–49, vol. 24, pp. 27–31). The method of Dickens and Massen for the estimation of cobalt in steels has been successfully applied to the estimation of cobalt in bright nickel-plating solutions. A sample of the plating solution is added to an excess of potassium ferricyanide, the excess of the latter being determined by titration with standard cobalt sulphate solution. The end point is determined potentiometrically using platinum and saturated calomel electrodes with a Cambridge *p*H meter as the measuring device.—R. A. R.

Determination of Impurities in Electroplating Solutions. XVI—Traces of Chloride in Copper Plating Baths. (Plating, 1950, vol. 37, Jan., pp. 62–66). Small quantities of chloride in copper-plating baths may be determined colorimetrically. The method depends upon the addition of a known quantity of silver ions and determining the excess of silver ions remaining after silver chloride has been precipitated. The excess is determined by the mixed colour of silver and dithizonate. Small amounts of lead, CrO_3, ferric iron, calcium, aluminium, sodium, nickel, silicon, or sugar do not interfere, and no separation of these impurities is necessary. The method is simple and rapid, and has an accuracy of 5%.—R. A. R.

Determination of Impurities in Electroplating Solutions. XVII—Traces of Lead in Copper Plating Baths. (Plating, 1950, vol. 37, Feb., pp. 166–170). In this method of determining lead in copper-plating baths the organic material is first oxidized with phosphoric acid. The lead is then separated from interfering ions by extracting with a CCl_4 solution of dithizone in the presence of KCN. After removal of the excess dithizone with alkaline KCN, the transmittance of the solution is measured and the quantity of lead determined from a calibration curve.—R. A. R.

PROPERTIES AND TESTS

Cohesion and Fracture in Metals. N. P. Allen. (Institution of Metallurgists, Jan., 1950, The Fracture of Metals, pp. 5–28). Theories for the fracture of metals are reviewed. The Taylor dislocation and the Griffith crack are explained, and plastic and brittle fractures and combinations of these are discussed.—R. A. R.

The Effects of Rate of Loading on Fracture of Materials. C. Gurney. (Institution of Metallurgists, Jan., 1950: The Fracture of Metals, pp. 101–116). Methods of testing at high rates of strain are described. The author's apparatus is one in which the test piece is attached to an elastic weigh-bar carrying four wire resistance strain gauges with a cathode-ray oscilloscope in the circuit. At the lower end of the test piece is attached a hanger carrying rubber pads. By dropping a weight on to the hanger, a specimen can be broken at a constant rate of loading in a period of 10^{-4} sec. The time to fracture can be increased by increasing the number of rubber pads. Results with this and other apparatus are discussed in three groups dealing respectively with the effect of the rate of loading on (*a*) the proof or yield strength, (*b*) the ultimate stress, and (*c*) deformation at fracture. Finally the theory of tensile impact is considered.—R. A. R.

Brittle Fracture of Mild Steel. W. Barr. (Institution of Metallurgists, Jan., 1950: The Fracture of Metals, pp. 117–138). The capacity of a steel to deform in the presence of a notch may be termed its notch ductility. Methods of determining notch ductility are described and some results discussed. Factors affecting notch sensitivity, and the ageing of steel are considered with special reference to plates.—R. A. R.

Notch Sensitivity of Mild Steel Plates. A. B. Bagsar. (Welding Journal, 1949, vol. 28, Oct., pp. 484-s–506-s). Several types of notched-bar tests, including tensile and bend tests as well as Charpy keyhole and **V**-notched tests were applied to a variety of steels in the form of plate of $\frac{1}{4}$ in. to $2\frac{1}{4}$ in. thickness. With steels in the as-received, normalized, water-quenched, or strain-aged condition, and with fractures transverse to the direction of rolling, transition temperatures determined by all the first three types of test agreed with one another. Within the thickness range $\frac{1}{4}$ in. to 1 in., the transition temperature as determined by the **V**-notch Charpy tests also agreed with these, but the temperatures given by the keyhole-notch Charpy tests were about 100° F. (56° C.) lower. There was no such agreement when the fractures were induced parallel to the direction of rolling, or when the steel was in the annealed condition. The first three types of test, known generically as cleavage-tear tests, are found to have advantages over impact tests, giving more information regarding notch sensitivity and the temperature T_n, at which yield and breaking strengths coincide, disclosing the anisotropic properties of steel plates, showing the effects of section thickness, and revealing the effects of heat-treatment on resistance to crack propagation.—J. P. S.

A Note on the Notch Effect of Metals. K. Minamiōzi and H. Okubo. (Journal of the Franklin Institute, 1950, vol. 249, Jan., pp. 49–55). Fatigue tests were conducted on round specimens of mild steel, high-tensile steel, and duralumin, each with a small transverse hole. The hole sizes varied between 0·0138 and 0·0787 in. The results showed that with these small holes the endurance limit decreased with increasing size of hole, which is contrary to the trend with larger sizes of hole, and a theory to account for this is advanced.—R. A. R.

Fracture by Fatigue. H. L. Cox. (Institution of Metallurgists, Jan., 1950, The Fracture of Metals, pp. 42–67). The nature of fatigue is discussed with many references to work carried out at the National Physical Laboratory. The subject is dealt with under the following headings: Introduction; The S–N Curve; Propagation of the Crack; Initiation of the Crack; Size Effect; Imperfection of Structure; Hypothesis as to the Nature of Fatigue; Conclusion.—R. A. R.

Meyer Analysis of Metals. H. M. Finniston, E. R. W. Jones, and P. E. Madsen. (Nature, 1949, vol. 164, Dec. 31, p. 1128). From equations connecting the load on a ball pressed into a plane surface for the determination of hardness with its diameter and the recovered diameter of the impression, it is made clear that the Mayer hardness *Pm* is a function of the shape of the impression. It is therefore decided that the ultimate ball hardness *Pu* when the ball is pressed up to its equator is the best value to represent the hardness of a

metal in a given condition. Here $P_u = (4aD^{n-2})/\pi$ where a is a constant for the metal, and also depends on the size of the ball, D is the diameter of the ball, and n is the Meyer index; for metals in general n is greater than 2. All previous work has been done on cubic metals and it has been found that P_u increases as n decreases; however, with magnesium, uranium, tin, zinc, and gallium, whose structures are not cubic, the correlation is positive, and the earlier interpretation of $(n - 2)$ as a measure of the work-hardening capacity of the metal should be reconsidered. This belief is substantiated by an examination of the relation between r, the coefficient of correlation between n and P_u, and the expansion anisotropy, which is a measure of the compression anisotropy. It is found that, whereas cubic materials are isotropic in this respect, the non-cubic materials show a strong positive relation between r and the anisotropy factor A_a, defined as $\alpha_{max} - \alpha_{min}/\alpha_{mean}$.—J. P. S.

Abrasive Wear of Metals. R. D. Haworth, jun. (Metal Progress, 1949, vol. 55, June, pp. 842–848). The effects of different abrading materials, speed, pressure, impact, moisture, and heat on the wear of metals, especially cast iron and steel, are discussed. Some of the factors affecting the performance and extent of abrasive wear of metals are reviewed and include particle size, the hardness of the abrasive and the roundness or angularity, the effect of speed in dry and wet abrasion, corrosion, and resistance to sliding abrasion.—J. C. R.

Ultramodern Supersonics and X-Rays. J. J. Pierce. (Metal Progress, 1949, vol. 56, July, pp. 62–65). An illustrated description is given of new X-ray and other non-destructive testing equipment at the Naval Ordnance Laboratory, White Oak, Md. The plant included a 10-million electron volt mobile betatron and a 2-million electron volt resonant X-ray generator, mounted on bridge cranes in a room with reinforced concrete walls 3 ft. thick. Reference is made to a method of electrostatic particle inspection patented under the name 'Statiflux.'—J. C. R.

Industrial Radiography. R. King. (Iron and Steel, 1949, vol. 22, Dec., pp. 633–635). Recommendations are made on safety precautions for X-ray, gamma ray, radium, and radon users.—R. A. R.

Determination of Residual Stresses by X-Ray Diffraction and Electric Extensometer. F. F. Pereira Pinto. (Boletim da Associacão Brasileira de Metais, 1947, vol. 3, July, pp. 452–489). [In Portuguese]. The author's personal experience with these two methods, both little used in Brazil, is described. The problem of residual stresses and its influence on everyday engineering problems is first discussed and the principles of the two methods are described. Precautions to be taken and the limitations of the methods are indicated. Practical applications described include the determination of stresses in quenched steel cylinders and in spot-welded ship plates.
R. S.

A Geiger Counter Spectrometer for the Measurement of Debye-Scherrer Line Shapes. W. H. Hall, U. W. Arndt, and R. A. Smith. (Proceedings of the Physical Society, Section A, 1949, vol. 62, Oct. 1, pp. 631–638). A spectrometer for the accurate measurement of X-ray powder-diffraction line intensities and shapes is described. Monochromatic radiation is used, and the diffracted beam intensity is recorded by a Geiger counter. The intensity of the X-ray source is monitored continuously, and errors due to variations in its output are automatically compensated. The accuracy and resolution obtainable are demonstrated by some typical experimental results.—R. A. R.

Creep Fractures. R. W. Bailey. (Institution of Metallurgists, Jan., 1950, The Fracture of Metals, pp. 29–41). Investigations of the nature of creep fractures, mostly in 0·5% molybdenum steels are reported.—R. A. R.

Critical Deformability of Cr–Mo–Si Alloy Steel for Superheater Tubes. W. Mielentz. (Brennstoff-Wärme-Kraft, 1950, vol. 2, Jan., pp. 9–13). An investigation of the causes of unusual cracks in low-alloy chromium–molybdenum–silicon steel superheater tubes is reported. The cracks had the following characteristics: (1) They were always at bends; (2) they were always longitudinal, and generally along the neutral axis of the bending plane; sometimes there was a second crack opposite the first, also along the neutral axis; there were occasionally additional cracks in the tension and compression zones at 90° from those in the neutral axis; (3) the cracks in the neutral zones began at the inner surface, the others at the outer surface; (4) there was no reduction in thickness at the crack edges. The state of stress leading to this damage appeared to arise when the tube was released after the bending operation. The trouble could be avoided by annealing at a temperature recommended by the tube makers.—R. A. R.

Metallographic Study of Heat Flow in Rocket Motor Walls. M. C. Sanz and H. C. Ihsen. (Metal Progress, 1949, vol. 56, Nov., pp. 685–687). In designing rocket motors it was necessary to determine the temperature gradient through a chromium–molybdenum steel wall (0·09 in. thick) of an orifice in which the gas-stream temperature rises to about 5000° F. in a fraction of a second. There is cooling water on the other side of the wall at 20 atm. which is heated to about 400° F. The metallographic method is based on using a micrograph of a section of the wall after the firing test to establish the position of the martensite–ferrite transition line, the hot side having been heated above the critical temperature and the cooled side having been kept below it. The temperature on the water-cooled side was calculated as 465° F. and a straight-line gradient was assumed, making the hot-side temperature about 2000° F. Possible sources of error are considered.—R. A. R.

Formation of 'Hair Line Cracks' by Hydrogen Introduced into Steel by Electrolysis. G. A. Geach. (Research, 1950, vol. 3, Feb., p. 98). Experiments are described in which a low-alloy nickel–chromium–molybdenum steel was soaked at 1300° C. oil-quenched, tempered at 710° C., heated and water-quenched from 1000° C., and finally tempered at 300° C. The specimen was cut into two equal cylinders, one of which was made the cathode in a bath of 1% H_2SO_4 and a current of 0·005 amp./sq. ft. passed for 10 days. The other cylinder received no further treatment. Thin discs were cut from each cylinder and etched. Radial cracks 1 to 3 mm. long were revealed near the circumference of the specimen treated in the electrolytic bath, but not in the control specimen. The results show that the quenching of an actual solution of hydrogen in steel need not be involved in any explanation of hair-line crack formation. They also suggest that thermal or transformation strains due to the quenching play only a secondary part in the process.—R. A. R.

On the Problem of Flakes in Steel. J. Novák. (Hutnické Listy, 1949, vol. 4, Oct., pp. 324–328). [In Czech]. Commenting on a paper by F. Kinský, the author states that methods of preventing flakes in steels recommended by individual authors apply only to a narrow range of conditions and may fail if conditions are different. Data are given on the influence of forging on flake formation and weldability of six different steels. Attention is drawn to the influence of weather on the formation of flakes in steel, *i.e.*, the influence of the season of the year. Investigations of N. M. Tschuiko and A. I. Lwowa (Stahl und Eisen, 1938, vol. 58, Nov. 10, p. 1297) are quoted and it is stated that the results obtained by them have been confirmed by investigations at the Skoda Works during 1947 and 1948. A graph summarizing these results is included.—E. G.

New Laboratory Concentrates on Steel Valve Research. (Steel, 1949, vol. 125, Nov. 7, pp. 122, 124, 150). At the East Chicago, Ind., plant of Edward Valves, Inc., a laboratory has been installed for high and low temperature creep, fatigue, impact, and hardness tests.—J. P. S.

Classification of Brazilian Pig Irons. R. F. de Azevedo. (Mineracão e Metalurgia, 1949, vol. 14, Sept.–Oct., Noticiario, pp. 3–4). [In Portuguese]. This draft plan for classifying pig irons was presented for discussion by the Brazilian Committee for the Classification and Standardization of Pig Irons. The system uses prefixes (in capitals) to indicate low and medium phosphorus, Bessemer, malleable, basic, and foundry irons. Six digits follow, the first three representing average silicon content, and the last three, sulphur. Suffixes (small letters) indicate chemical modifications. Tables showing analyses and uses of the various irons are given.
R. S.

METALLOGRAPHY

Fractographic Structures in Weld Metal. C. A. Zapffe and C. O. Worden. (Welding Journal, 1949, vol. 28, Nov., pp. 527-s–533-s). The authors have applied their 'fractographic' technique (*see* Journ. I. and S.I., 1949, vol. 163, p. 475) to the study of weld metal; specimens from the middle third of

right-angle fillet welds were fractured by hammer blow either at room temperature or at the temperature (— 196° C.) of liquid nitrogen. They conclude that fractography is applicable to weld fractures and that the toughness of weld metal can be given a useful qualitative rating on the basis of the fractographic pattern. They then apply the technique to a study of the electrodes E 6010, E 6015, and E 6020, concluding that the first is inferior to the others, and that imperfectly dried E 6015 is no better than E 6010; if E 6015 is properly dried—and a 'short circuit' drying just before welding may further improve its qualities—it is the best of the three. E 6020 produces only slightly inferior weld metal. Type E 6012, which was also studied, produces large and flat facets, indicating markedly inferior toughness; type E 6015 with added phosphorus gives a highly inferior fracture pattern.

J. P. S.

Ingot Iron Inside Out. C. A. Zapffe and C. O. Worden. (Metal Progress, 1949, vol. 56, Nov., pp. 672–673). The 'obverse and reverse' patterns of a single cleavage traverse through an individual grain in ingot iron are reproduced side by side as two fractographs at 350 diameters. Minute round pockets are probably caused by the high pressure of hydrogen which apparently blasts tiny blocks of metal from the newly formed cleavage surfaces at the instant of fracture. Much of the detail in the two fractographs is exactly symmetrical; some is slightly altered, and certain markings are sharply defined on one face but do not appear at all on the other.

R. A. R.

Investigating the Structure of Metals with the Aid of "Electrolytic Spot Etching." G. Stähli and W. Rüegg. (Schweizer Archiv, 1950, vol. 16, Jan., pp. 25–27). A simple apparatus is described for the rapid electrolytic polishing and etching of small areas on metallographic specimens. A glass vessel containing the electrolyte ($C_2H_5OH + HClO_4 + H_2O$) is connected by a tube to a vertical glass tube with a 2-mm. dia. opening at the bottom through which protrudes the cathode consisting of a 1-mm. dia. copper wire. The specimen is the anode and it lies on an insulated platform 1–3 mm. below the end of the copper wire. The tap below the electrolyte reservoir is turned on and the current is switched on for a few seconds, and this is sufficient to produce a small circular polished area on the specimen.—R. A. R.

Ferric Chloride Etchant for Austenite Grain Size of Low-Carbon Steel. O. O. Miller and M. J. Day. (Metal Progress, 1949, vol. 56, Nov., pp. 692–695). A list of ten etchants for revealing austenite grain size in rapidly quenched low-carbon steels is given, and the procedure for preparing the specimen and etching with an aqueous solution of ferric chloride, which gives excellent results, is described in detail.—R. A. R.

A Contribution to the Problem of Non-Metallic Inclusions in Steel. V. Zedník. (Hutnické Listy, 1949, vol. 4, Oct., pp. 319–324; Nov., pp. 360–363). [In Czech]. Qualitative and quantitative determination of inclusions in steel is only possible by combining metallographic, extraction, microchemical, and cathode-ray methods. To obtain data for further research work on non-metallic inclusions, tests have been carried out in the Research Laboratories of the Vitkovice Steelworks. The non-metallic inclusions in several typical heats of steel were analysed by the modified Dicken's method and by microchemical and cathode-ray methods. Five mechanically separated relatively large non-metallic inclusions, and two specimens from a faultless test bar were examined. The results of microanalysis of these inclusions are given. The MnO and FeO contents of forged test pieces and of specimens cast direct from the ladle into ingot moulds have also been determined in order to obtain data on the variation of the content of these oxides resulting from the relatively large surface of the molten metal in contact with the air during the casting process. There was not much difference between the analyses of very fine and of relatively large inclusions, which indicates that the process of their formation is the same. The relatively high CaO and MgO contents indicate that the inclusions are partly due to corrosive and erosive action of the steel on the furnace lining. Deoxidation has only an indirect influence, or none at all, on the formation of non-metallic inclusions, but it does affect the viscosity of the steel. Inclusions obtained from deoxidized cast specimens were high in SiO_2 and contained no CaO or MgO, whilst the Al_2O_3 content depended on the method of deoxidation. Micrographs are presented to show the manner in which inclusions in steel deoxidized with calcium silicide reacted with etching reagents.—E. G.

CORROSION

Corrosion of Cadmium and Zinc Coatings in Electrical Equipment. P. T. Gilbert and S. E. Hadden. (Journal of the Electrodepositors' Technical Society, 1950, vol. 25, pp. 41–49). Laboratory tests were made to determine the behaviour of cadmium and zinc coatings at room temperature and at 60° C. in humid atmospheres in the presence and absence of various insulating materials. The results indicate that cadmium plating, particularly if chromated, should give adequate protection to steel components in electrical equipment in most conditions of exposure even when temperatures and relative humidities are high.—R. A. R.

Corrosion Cracking. U. R. Evans. (Institution of Metallurgists, Jan., 1950: The Fracture of Metals, pp. 68–100). The author reviews corrosion from the chemical, electrochemical, and crystallographic angles; he then considers the effect of stress and leads up to a theoretical picture of corrosion cracking. Some practical examples are described, and finally, methods of preventing corrosion are suggested.

R. A. R.

Report of Subcommittee XV on Field Tests of Wire and Wire Products. (Proceedings of the American Society for Testing Materials, 1949, vol. 49, pp. 113–127). This report summarizes the results of atmospheric corrosion tests on bare steel and zinc-coated wires and wire products, and on some copper and lead-coated steel wires at locations in the United States representing industrial, rural, and sea-coast atmospheres. Most of the results are given in tabular form with code letters indicating the nature and appearance of the corrosion product.—R. A. R.

Report of Subcommittee II on Performance Tests. (Proceedings of the American Society for Testing Materials, 1949, vol. 49, pp. 220–238). This report is in two parts. The first part summarizes the results of the atmospheric exposure of electroplated lead coatings on steel. The second part gives the results of atmospheric exposure of electrodeposits of chromium on nickel on copper on high-carbon steel.—R. A. R.

An Electron Diffraction of the Surface of Iron which Has Been Eroded by an Explosive. T. Katsurai and S. Yamaguchi. (Bulletin of the Institute of Physical and Chemical Research, vol. 22, No. 8, pp. 750–751). [In Japanese].

Oxidation of Iron in the Range 200°–400° C. (Nature, 1949, vol. 164, Nov. 26, pp. 909–911). **Investigations at Cambridge.** U. R. Evans. (Pp. 909–910). **Investigations at Teddington (Oxidation of Iron Around 200° C.).** W. H. J. Vernon, T. J. Nurse, C. J. B. Clews, and E. A. Calnan. (Pp. 910–911). The first of these two papers describes work carried out at the Department of Metallurgy, Cambridge, on the formation of oxide films on iron. From study of films produced on iron containing 0·02% carbon and 0·04% oxygen as a magnetite network, Dr. Evans concludes that phenomena observed earlier by W. H. J. Vernon indicate that below 200° C. there is insufficient energy for the formation of nuclei at points on the surface, so that oxidation must either go on at places where oxide nuclei already existed or at places of atomic disarray where little energy is required for the formation of nuclei. Local or internal oxidation such as this would be unfavourable to the development of interference colours and inconsistent with parabolic growth, the two factors Vernon found lacking below 200° C. Above 200° C., however, nuclei form spontaneously at the surface, and a uniform film develops, productive of interference colours and thickening by a parabolic law. The two phenomena set in, however, at the same temperature on materials containing no internal point of disarray, thus accounting for the growth, slow though it may be, of films at low temperatures on single crystals and polished surfaces. In the second communication, Vernon and his coworkers at Teddington describe their studies of stripped films by electron diffraction in relation to the same phenomena. They confirm that while at 180° C. no progression of interference colours is noted, and at 225° C. it is, the films produced at both temperatures consist of an outer layer of rhombohedral α–Fe_2O_3 which overlies a cubic oxide of composition between γ–Fe_2O_3 and Fe_3O_4; there is, therefore, no major crystalline change at the critical point where parabolic growth begins.

Chemical analysis shows that even for very extended periods, up to 453 hr. of heating at 180° C. the values of ferric and total iron remain approximately constant : therefore there is no increase in the thickness of the film which can be stripped, and, as it is a fact that oxygen is being absorbed nonetheless, it must be adding to the content of iron oxide beneath the film, in the zone of " iron oxide incorporated sporadically in a matrix of iron," described earlier by Vernon, Wormwell, and Nurse (*see* Journ. I. and S.I., 1939, No. II, p. 179A). At 225° C., however, the uptake of oxygen does contribute directly to the thickness of the film, as its total oxygen content shows. The authors therefore conclude that the mode and rate of growth of the film depend on the rate of diffusion of oxygen, whether as ions, atoms, or molecules, through the outer rhombohedral zone, and of ions of iron through the inner cubic zone : the temperature coefficients of these are likely to differ. Evidence suggests that the curve for the second process is steeper than that for the first and that they intersect at about 200° C. Thus, below 200° C. oxidation is propagated by diffusion of oxygen inwards, and above 200° C. by diffusion of iron outwards. The relative diffusion rates will, however, depend very appreciably on the initial surface condition of the metal, the value of 200° C. being characteristic of polycrystalline surfaces prepared by ' abrasion '—not polishing. The critical value will be lower, as Dr. Evans' contribution remarks, for single crystals and for polished surfaces. Finally, whereas the diffusion of iron ions outwards must produce new oxide at the outer interface, the diffusion of oxygen inwards brings the atoms into contact with the mixed assembly of iron and magnetic oxide nuclei, and oxidation will proceed by the growth of these nuclei rather than by film thickening. This is a conclusion similar to that reached by Dr. Evans by a different mode of approach.

J. P. S.

ANALYSIS

Photoelectric Colorimetry. R. F. Muraca. (Plating, 1950, vol. 37, Jan., pp. 53–58, 68). The development of a photoelectric colorimeter from the simple circuit consisting of a lamp, photocell, and galvanometer to a differential photocell circuit is described. A brief discussion of the use of filters and of errors arising in colorimetry is followed by descriptions of turbidimeters, nephelometers, and fluorophotometers.

Contribution to the Quantitative Determination of Phosphorus Segregation in Iron and Steel by Contact Printing. H. Grubitsch and P. Warbichler. (Berg- und Hüttenmännische Monatschefte der Montanistischen Hochschule in Leoben, 1950, vol. 95, Jan., pp. 16–18). The authors have previously described a process for making phosphorus prints on cellophane (*see* Journ. I. and S.I., 1946, No. I, p. 15A). The object of the present investigation was to ascertain whether the colour intensity of the print was related to the phosphorus content. The colour intensities were measured by an electric microcolorimeter, and it was found that the extinction plotted against the phosphorus content on a logarithmic scale gave a straight line. Tests on sections of rail and a large crankshaft proved that the phosphorus segregation in steel could be quantitatively determined quite accurately.—R. A. R.

Hot-Extraction Method of Gas Analysis as Applied to Cast Iron. J. E. Hurst and R. V. Riley. (Proceedings of the Institute of British Foundrymen, 1949, vol. 42, pp. A185–A191). The paper is a progress report on the technique and results obtained by the hot-extraction method of gas analysis applied to cast iron. It is evident that the mechanism governing the evolution of hydrogen from cast iron on heating *in vacuo* is far from simple. The composition of the gas evolved at 600–800° C. *in vacuo* is not predominantly hydrogen ; it contains appreciable amounts of nitrogen and carbon monoxide. Treatment at this temperature does not remove all the gases present. As a broad conclusion, there is a strong possibility that the total oxygen content, as found by vacuum-fusion analysis of grey cast iron, is not a measure of the inclusions of oxides and silicates present. The oxygen content is due in part, at least, to the presence of carbon monoxide existing either in voids in the iron or in close association with the flake graphite. The distribution of nitrogen in iron is probably also complicated by the presence of graphite and a more open structure than is found in a wrought metal such as steel.—R. A. R.

Steel Analysis Time Cut by Radio Frequency Heating. W. K. Aites. (Steel, 1949, vol. 125, Dec. 12, pp. 92–93, 112). The technique of making carbon and sulphur determinations by the combustion method has been improved by using induction heating ; the apparatus for this is described. The sample is melted in a short vertical glass combustion tube surrounded by an air-cooled coil to which radio-frequency energy is supplied by a vacuum tube oscillator. The conventional boat is replaced by a refractory ' cupelet ' developed specially to withstand the thermal shock. With oxygen flow at 600–700 c.c./min. complete fusion of a 0·5-g. sample was obtained within 40–60 sec. from time of ignition, the time for carbon analysis was reduced from 10 min. to 2½ min.

Melting Control with the Direct-Reading Spectrometer. E. R. Vance. (American Institute of Mining and Metallurgical Engineers, Electric Furnace Steel Conference Proceedings, 1949, vol. 7, pp. 107–110 : Journal of Metals, 1949, vol. 1, Oct., pp. 28–30). Particulars are given of the use of the direct-reading spectrometer for analytical control in electric furnace practice at the plant of the Timken Roller Bearing Co., Canton, Ohio. The instrument is located in an air-conditioned room which is maintained at a temperature of 75° F. and 50% relative humidity. In the direct-reading spectrometer, the photographic stage has been entirely replaced by sensitive photo-multiplier tubes, which pick up the emitted light from the elements at the various wavelengths and report it as a percentage on calibrated clock dials within 30 sec. after a sample has been placed in the electrode holders.—R. E.

Identification of Aluminium Nitride in Steels Deoxidised with Aluminium. (Electron Diffraction Method). T. Tokumitu. (Bulletin of the Institute of Physical and Chemical Research, vol. 21, No. 2, pp. 89–94). [In Japanese].

MISCELLANEOUS

The Lay in Parallel-Lay Spiral Wire Ropes to Prevent Crossing of the Wires at Their Points of Contact. H. Herbst. (Stahl und Eisen, 1950, vol. 70, Jan. 5, pp. 26–30). In order to avoid the formation of wear channels and the high bending stresses at the points where the wires in a wire rope cross, a method of parallel ' lay ' has been devised which is described.

R. A. R.

New Ways of Making Wire Ropes. K. Wolf. (Stahl und Eisen, 1950, vol. 70, Jan. 19, pp. 63–66). The different ' lays ' used in the making of wire ropes are explained, special reference being made to the new parallel lay.—R. A. R.

BOOK NOTICES

INSTITUTION OF METALLURGISTS. " *Metals in the Service of Mankind.*" Exhibition held at the Science Museum, London, July to September, 1950, 8vo. pp. 137. London, 1950 : The Institution of Metallurgists. (Price 1*s.*)

The exhibition to which this handbook relates was organized primarily with the object of revealing to the public in general, and to young people in particular, something of the story of the many metals and alloys which are in use today for an almost infinite variety of purposes.

The first part of the book sets out the purpose of the exhibition and an outline of the content of each display, and thus forms a guide to the visitor. In the second part the story of metals is told in non-technical language in a series of eleven chapters covering the history of the production of metals from ores, refining, shaping, processing, treatment of metal surfaces, and control and research. Chapters on the precious and uncommon metals are included.—R. A. R.

INSTITUTE OF METALS. " *Metallurgical Applications of the Electron Microscope.*" A Symposium held at the Royal Institution, London, on 16 Nov., 1949. (Institute of Metals. Monograph and Report Series No. 8). 8vo, pp. vi + 164. Illustrated. London, 1950 : The Institute of Metals. (Price £1. 1*s.*)

This monograph contains thirteen papers presented at a Symposium held at the Royal Institution, London, on November 16, 1949, and the discussion upon them. The Symposium was organized by the Institute of Metals in association with the Chemical Society, the Faraday Society, the Institute of Physics, the Institution of Electrical

Engineers, The Iron and Steel Institute, the Physical Society, and the Royal Microscopical Society. The following papers were contributed by leading American, British, French, and German scientists: The Application of the Electron Microscope in Metallography, by N. P. Allen; Electron Microscopy in Metallurgy, by P. Grivet; The Use of the Electron Microscope in Metallurgical Research in Germany During and Since the War, by H. Mahl; The Structure of Some Non-Ferrous Alloys as Revealed by the Electron Microscope, by G. L. J. Bailey and Sheila Vernon-Smith; A Replica Technique for the Examination of Fracture Surfaces with the Electron Microscope, by J. Nutting and V. E. Coslett; The Dry Stripping of Formvar Replicas from Etched Metal Surfaces, by J. Nutting and V. E. Coslett; The Microstructure of a Water-Quenched Carburized Iron, by J. Trotter, D. McLean, and C. B. J. Clews; Electron Microscopy of Light-Metal Alloys, by F. Keller; Observations on the Age-Hardening Process in an Aluminium–Copper Alloy, by G. L. Bucknell and G. A. Geach; Elementary Slip Processes in Aluminium as Shown by the Electron Microscope, by A. F. Brown; Studies in the Electron Microscopy of Nickel–Chromium Alloys, by B. S. Cooper and G. A. Bassett; A Note on the Examination of Metal Powders by the Electron Microscope, by J. I. Morley; and The Progress of Electron Microscopy of Metals in America (Excluding the Light Metals), by C. M. Schwartz.

The book contains 50 excellent plates of electron micrographs.—R. A. R.

INSTITUTE OF FUEL AND INSTITUTE OF PETROLEUM. "*Modern Applications of Liquid Fuels.*" Report of a Joint Conference held by the Institute of Fuel and The Institute of Petroleum at the University of Birmingham, September 21–23, 1948. 8vo, pp. viii + 495. Illustrated. London, 1950. (Price £1. 1*s.*)

The idea of holding a conference to discuss the modern application of liquid fuels arose in 1947 during the fuel crisis in Great Britain. The scope of the conference was designed to cover the industrial uses of all liquid fuels except the lightest fractions.

Apart from the opening address by the President, J. A. Oriel, on The Place of Liquid Fuel in British Economy, the papers are arranged in groups of two or three according to the industries in which the fuel is used; these include steel and metals, glass and ceramics, gas turbines, Diesel engines for power generation and railway traction, agriculture, gas-making, and domestic heating.

The papers of ferrous interest are: Oil-Fired Open-Hearth Furnaces: A Review of British Practice, by T. C. Bailey; The Open-Hearth Furnace—A Comparison of Oil and Producer Gas Firing, by I. M. D. Halliday; Fuel Oil in the Steel Industry of the U.S.A., by A. J. Fisher; and The Use of Fuel Oil in Furnaces for the Iron and Steel Fabricating Industries, by M. Roddan.—R. A. R.

"*Gmelins Handbuch der anorganischen Chemie.*" 8 Aufl. System-Nummer 18. "*Antimon.*" Teil B. Lieferung 3. "*Schluss der Verbindungen.*" 8vo, pp. xxi + xvi + 497–564. Clausthal-Zellerfeld, 1949: Gmelin-Verlag, G.m.b.H. (Price DM 24.75)

The two previous handbooks covered the element antimony and its compounds up to antimony and iodine, whilst the present work covers the remainder of the compounds. The thorough manner in which the literature has been searched and the information classified can be appreciated by taking a compound at random. It will be found, for example, that 22 pages are devoted to antimony trisulphide, and that the data are classified under: Composition, formation and preparation, special forms, heat of formation, physical properties, electrochemical behaviour, and chemical behaviour. It is stated in the introductory matter that about 2200 journals have been examined in the course of compiling this work, and an alphabetical list is given of those most frequently cited. A very comprehensive list of contents facilitates rapid reference to information on any property of any of the compounds included in the handbook.—R. A. R.

DAVIES, MAX. "*The Story of Steel.*" 4to, pp. 96. Illustrated. London, 1950: The Burke Publishing Co., Ltd. (Price 7*s.* 6*d.*)

This book is not so much addressed to metallurgists as to steel users, and to anyone interested in the product of the greatest of our basic industries. It is, however, written in such an interesting way that many people disinterested in metallurgy or steel as a basic industry will nevertheless read it with pleasure.

The first part of the book deals with the history of steel from the very earliest days right up to modern times. The latter portion of the book is devoted to a description of the blast-furnace and the various steelmaking processes. Each section is illustrated by photographs of modern plant and by a series of remarkably clear diagrams which well illustrate the principles of the various processes.

J. FERDINAND KAYSER.

NEW PUBLICATIONS

AMERICAN IRON AND STEEL INSTITUTE. "*Annual Statistical Report* 1949." 8vo, pp. iv + 106. New York, 1950: The Institute.

AMERICAN SOCIETY FOR METALS. "*Thermodynamics in Physical Metallurgy.*" 8vo, pp. vii + 319. Illustrated. Cleveland, Ohio, 1950: The Society. (Price $5)

BEECHING, R. "*Electron Diffraction.*" Second edition. New York, 1950: John Wiley and Sons. (Price $1.25)

BRITISH STANDARDS INSTITUTION. B.S. 1453: 1950. "*Steel Filler Rods for Gas Welding of Mild Steel.*" 8vo, pp. 50. London: The Institution. (Price 1*s.*)

COMSTOCK, G. F. "*Titanium in Steel.*" Pp. 328. New York: Pitman Publishing Corp. (Price $7.50)

COSLETT, V. E. "*Introduction to Electron Optics; the Production, Propagation and Focusing of Electron Beams.*" Second Edition. 8vo, pp. xvi + 294. Illustrated. London, 1950: Oxford University Press. (Price 27*s.* 6*d.*)

ECKMAN, D. P. "*Industrial Instrumentation.*" Pp. vi + 396. New York: John Wiley and Sons, Inc. (Price $5)

GUTHRIE, A. and R. K. WALKERLING. "*Vacuum Equipment and Techniques.*" (National Nuclear Energy Series, Manhattan Project Technical Section, Division 1, vol. 1). 8vo, pp. 264. London, 1950: McGraw-Hill Publishing Co., Ltd. (Price 21*s.* 6*d.*)

GWIAZDOWSKI, A. P. "*Engineering Metallurgy.*" Pp. 246. Appleton, Wis.: C. C. Nelson Publishing Co. (Price $4)

HARVEY, C. E. "*Spectrochemical Procedures.*" Pp. 402. Detroit, Mich.: Applied Research Laboratories. (Price $7.50)

JAMES, R. W. "*X-Ray Crystallography.*" (Methuen's Monographs on Physical Subjects). Fourth Edition. 8vo, pp. 88. London, 1950: Methuen and Co., Ltd. (Price 4*s.* 6*d.*)

LANG, M. "*Prüfen der Zerspanbarkeit durch Messung der Schnittemperatur.*" Pp. 119. Munich, 1949: Carl Hanser Verlag. (Price DM 8.20)

MANCHESTER JOINT RESEARCH COUNCIL. "*Operational Research. Its Application to Peace-Time Industry.*" 8vo, pp. 150. Manchester: Manchester Joint Research Council. (Price 10*s.* 6*d.*)

MINISTRY OF SUPPLY. ATOMIC ENERGY RESEARCH ESTABLISHMENT. "*Radioactive Tracers in Metallurgical Research.*" By W. S. Eastwood, W. G. Marley, H. M. Finniston, and A. E. Williams. 8vo, pp. 55. London, 1950: H.M. Stationery Office. (Price 1*s.* 6*d.*)

MOOD, A. M. "*Introduction to the Theory of Statistics.*" 8vo, pp. 433. London, 1950: McGraw Hill Publishing Co., Ltd. (Price 42*s.* 6*d.*)

PATTERSON, A. M. "*German-English Dictionary for Chemists.*" 3rd Edition. New York: John Wiley and Sons, Inc. (Price $5).

SEARLE, A. B. "*Refractory Materials: Their Manufacture and Use.*" Third Edition, second impression. 8vo, pp. xvi + 895. London, 1950: Charles Griffin and Co., Ltd. (Price 45*s.*)

STANLEY, W. A. "*Resistance Welding, Designing, Tooling, and Applications.*" New York: McGraw-Hill Book Co., Inc.; London: McGraw-Hill Publishing Co., Ltd. (Price 64*s.*)